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THE THERMOELECTRIC POWER OF SOME RESISTANCE MINIMUM ALLOYS

by

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A THESIS

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The undersigned certify that they have read,
and recommend to the Faculty of Graduate Studies for
acceptance, a thesis entitled THE THERMOELECTRIC POWER
OF SOME RESISTANCE MINIMUM ALLOYS submitted by Howard
Malm in partial fulfilment of the requirements for the
degree of Master of Science.

ABSTRACT

Alloys of silver with small amounts of manganese (0.31 atomic percent or less) were prepared. Experiments to measure the electrical resistivity, thermal conductivity, and thermoelectric power of these alloys are described. Effects were observed in the thermal conductivity and the thermoelectric power associated with the minimum and maximum that occur in the electrical resistivity below 30°K. The results are interpreted in terms of possible electron scattering mechanisms, particularly in terms of a model advanced by Kondo (1964a, 1964b). Reasonably good agreement with Kondo's model is obtained for the measured electrical resistivity and the thermoelectric power.

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INTRODUCTION

Normally the electrical resistivity of pure metals and many dilute alloys may be written as $\rho = \rho_0 + \rho_i(T)$ where $\rho_i(T)$ is the electrical resistivity from scattering of electrons by lattice waves and ρ_0 is from scattering of electrons by lattice imperfections and impurity atoms. At low temperatures where $\rho_i(T) \ll \rho_0$, the electrical resistivity is constant. However experiments at Leiden about 30 years ago showed that certain samples of the noble metals exhibited a minimum in the electrical resistivity at low temperatures ($< 30^\circ\text{K}$). It was subsequently found that small amounts of certain transition metals in solid solution in the noble metals produced this resistance minimum and sometimes at still lower temperatures a resistance maximum.

Associated with this unusual behavior of the electrical resistivity is an even more striking departure of the thermoelectric power of such alloys from that of a pure metal. At low temperatures the thermoelectric power of certain dilute alloys may be more than 100 times greater than the thermoelectric power of a pure metal.

The theoretical situation with respect to resistance minimum alloys is presently in an unresolved

state. Although the transport properties of pure metals and dilute alloys with non-transition metal impurities can be adequately described, alloys with transition metal impurities are not well understood.

In an attempt to separate the conduction mechanisms involved in resistance minimum alloys, we made thermal and electrical measurements on several samples of silver with different, small amounts of manganese in solid solution. Each sample was mounted in a cryostat where the electrical resistivity, thermal conductivity and thermoelectric power could be measured at the same time in the temperature range 2 to 25°K.

Measurements such as these, covering the full temperature range 2 to 25°K have been published only for a very few alloys.

The thesis is divided into four major sections. The first section is an outline of the basic theory of the transport properties of a metal. A review of the scattering problem in relation to the Boltzmann equation is included as well as a brief review of the various models that have been used in attempts to explain the electrical and thermal properties of resistance minimum (and maximum) alloys. The cryostat and instruments used for the measurements together with specimen preparation are described in the second

section. The third section consists of tables and graphs of the experimental measurements. The last section contains a discussion of the results and an explanation of or a possible explanation of the results. An appendix deals with the calibration procedure necessary for thermoelectric power measurements.

PART I THEORY

I.1 General

The temperature independent electrical resistance that is produced by static imperfections in the lattice and is characteristic of pure metals and many alloys at low temperatures is often referred to as the residual resistance. The addition of a non-magnetic impurity to a pure metal increases the residual resistance by an amount proportional to the impurity concentration but leaves the electrical resistance temperature independent at low temperatures (see figure 1). However the addition of small amounts of certain transition metal (magnetic) impurities to gold, silver, copper and some other metals produces a resistance minimum (and sometimes a resistance maximum) at low temperatures. The thermal conductivity λ increases monotonically with temperature at low temperatures in normal metals. There are effects in the thermal conductivity associated with anomalies in the electrical resistance. Also associated with the unusual behavior of the electrical resistivity is an anomalously large thermoelectric power.

Let us first discuss certain aspects of the theory describing the transport properties of metals. A complete discussion can be found in various standard works

such as Mott and Jones (1936), Wilson (1953) and Ziman (1960, 1961).

If some of the details of the scattering of the conduction electrons are known, then one can calculate the electrical and thermal resistivities and the thermoelectric power as a function of temperature from the Boltzmann transport equation

$$\frac{\partial F}{\partial t} + \nabla_z F \cdot \vec{v} + \nabla_v F \cdot \dot{\vec{v}} = \left(\frac{\partial F}{\partial t} \right)_{\text{coll}} \quad (1)$$

where F is the electron distribution function, $\vec{v}$ is the electron velocity, and $\left(\frac{\partial F}{\partial t} \right)_{\text{coll}}$ is the rate of return to an equilibrium distribution by collisions.

In the residual resistance region, where lattice imperfections and impurity atoms act as simple screened potential scatterers, a relaxation time τ may be used in solving the Boltzmann equation. The use of a relaxation time implies elastic collisions of electrons (electron energy is conserved) with the scatterers. Then, solving the Boltzmann equation gives

$$\begin{aligned} \rho_0 &= \text{constant}, \\ W_e &= \frac{\text{constant}}{T}, \end{aligned}$$

where ρ_0 is the residual electrical resistivity and T

is the absolute temperature. W_e is the electronic thermal resistivity (the inverse of the electronic thermal conductivity) or in other words the resistance to the transport of heat experienced by the electrons. The Lorenz relation also known as the Wiedemann-Franz law states that the quantity $\rho_0/W_e T$ is constant. The theoretical Sommerfeld value of the Lorenz number L_0 is given by

$$\begin{aligned} \frac{\rho_0}{W_e T} &= L_0 = \frac{1}{3} \frac{\pi^2 k^2}{e^2} \\ &= 2.45 \times 10^{-8} \frac{\text{watt ohm}}{\text{deg}^2} \end{aligned} \quad (2)$$

The existence of a relaxation time for elastic scattering means that the Lorenz ratio should be constant, whatever the shape of the Fermi surface and the precise form of the scattering function.

At higher temperatures where scattering of electrons by phonons or lattice waves is becoming important, the electrical and thermal resistivities both increase rapidly with temperature although not in the same manner. At temperatures above the Debye temperature θ of the lattice

$$\lambda \rightarrow \text{constant}$$

$$\text{and } \rho \propto T.$$

When inelastic scattering terms (electron energy not conserved) are included, the thermal and electrical resistivities will not in general be affected in the same way. A deviation from a constant Lorenz number is expected when there is inelastic scattering of the conduction electrons at a temperature less than the Debye temperature θ .

The conduction mechanisms in the pure noble metals seem to be fairly well understood (Ziman (1961)). The addition to a pure metal of an impurity in dilute concentrations (less than 1 part in 100) introduces a known number or type of scattering centers for the conduction electrons. The study of the transport properties may in this sense be considered as a study of the various kinds of scattering due to the impurity ion.

Certain specimens of the noble metals were found by de Haas and Van den Berg (1936) to exhibit a resistance minimum at low temperatures. This effect was attributed to impurities. Much work has been done since then on resistance minimum alloys. For example see Gerritsen and Linde (1951), MacDonald and Pearson (1953) and Gerritsen (1959). It was not until 1960 that Gold et al (1960) showed that the resistance minimum was due to a magnetic impurity such as Fe or Mn and not due to a non-magnetic impurity such as Ge or Sn.

The difference between a magnetic and non-magnetic impurity is the "spin" arising from the unpaired 'd' or 'f' electron in the magnetic ion. Thus one can say generally that an interaction between the spin or 'd' electron(s) of the impurity ion and the conduction electrons is responsible for the unusual behavior of the resistance in resistance minimum (and maximum) alloys.

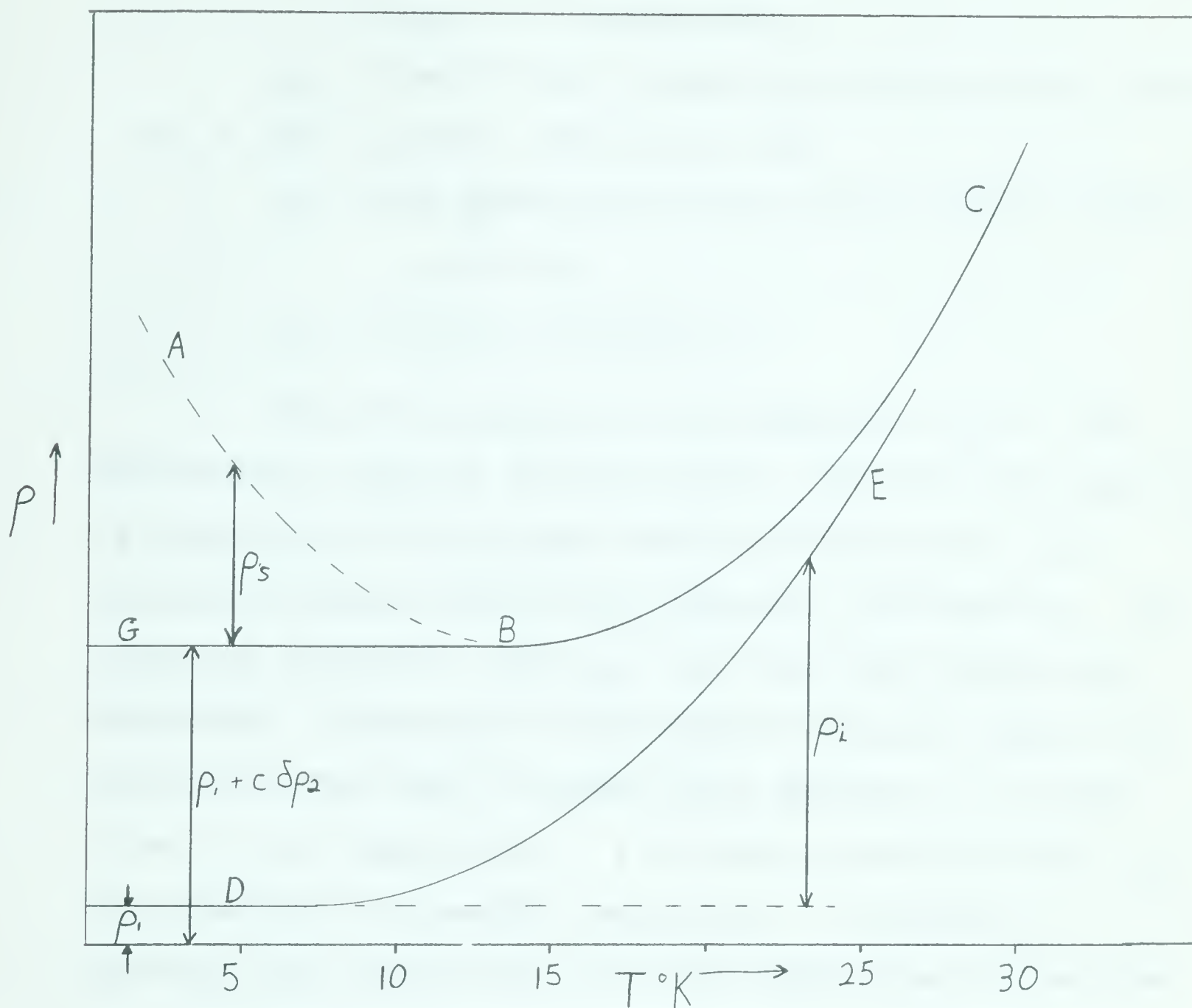
The following gives a brief outline of the effect of an impurity on the transport properties.

I.2 Electrical Resistivity

The resistivity of a perfectly periodic lattice at the absolute zero of temperature is ideally zero (Mott and Jones (1936)). In practice in a pure metal the perfect periodicity is disturbed by dislocations, vacancies, and impurities. The addition of an impurity also disturbs the lattice periodicity. As the temperature of the lattice (and electrons) rises, the lattice waves contribute a temperature dependent term to the resistivity. Using Matthiessen's rule which says the above contributions to the resistivity may be added algebraically one has

$$\rho_T = \rho_0 + \rho_i + \rho_s \quad (3)$$

$$= \rho_1 + \delta\rho_2 c + aT^5 + \rho_s \quad (T < \theta)$$



- T - temperature
- ρ_i - ideal resistivity
- ρ_s - anomalous resistivity
- ρ_1 - residual resistivity of pure silver
- $c \delta \rho_2$ - impurity resistivity
- C - concentration of impurity

Figure 1

Electrical Resistivity of Metals

ρ_1 - resistivity of the pure metal

c - impurity concentration

$\delta\rho_2$ - resistivity increase per atomic percent impurity

$\rho_i = aT^5$ - lattice resistivity term

ρ_s - any departure from the simple theory already outlined

ρ_0 - residual resistivity .

When the impurity is non-magnetic $\rho_s = 0$ and Matthiessen's rule is closely obeyed. Even when the impurity is magnetic, the additional residual resistance at the minimum is proportional to the impurity concentration. The anomalous resistance term ρ_s has a peculiar temperature dependence. Depending on the magnetic impurity added, the resistivity may have a minimum and a maximum or a minimum alone at low temperatures. A minimum is produced when ρ_s decreases with increasing temperature. A maximum is produced at a temperature below the resistance minimum when ρ_s increases with increasing temperature. This behavior of ρ_s could conceivably reflect a disordering process.

The electrical resistivity ρ obtained by solving the Boltzmann equation is given by

$$\frac{1}{\rho} = \sigma = \frac{e^2}{12\pi^3} \int \tau_K V_K^2 \left(\frac{dF_0}{dE_K} \right) d^3K \quad (4)$$

where $V_K = \hbar k/m$. τ_K is the characteristic relaxation time of an electron with wave vector $\vec{K}$; dF_0/dE_K is the derivative of the Fermi distribution function and is non-zero only near the Fermi energy E_F . The integration is over all of K space. The relaxation time τ , often assumed to be constant, may be a function of electron energy, in which case the conductivity σ may be a function of temperature. The finding of a suitable relaxation time $\tau_K(E)$ is essential to give a temperature dependence to the conductivity σ . Of course finding $\tau_K(E)$ requires some knowledge or assumptions about the scattering of conduction electrons. Any theory which explains the resistance minimum and maximum must explain them in terms of temperature dependent scattering terms.

I.3 Thermal Resistivity

There is an extra complication in the thermal conductivity in that heat is conducted by both the lattice and the conduction electrons. If we assume these processes take place independently we can write

$$\lambda = \lambda_g + \lambda_e \quad (5)$$

where λ is the total thermal conductivity, λ_g is the lattice conductivity, and λ_e is the electronic conductivity.

The electronic thermal resistivity ($1/\lambda_e$) consists of algebraically additive parts (Matthiessen's rule).

$$\begin{aligned} \frac{1}{\lambda_e} &= W_e = W_o + W_i \\ &= \frac{A}{T} + BT^2, \end{aligned} \quad (5a)$$

where W_o is the impurity resistivity, W_i is the ideal lattice resistivity. In the low temperature limit $A = \rho_o/L$ with elastic scattering and B is characteristic of electron-phonon interaction.

The electronic thermal conductivity λ_e is given by

$$\begin{aligned} \lambda_e &= - \frac{k^2 T}{36\pi} \int \tau_K V_K^2 \left(\frac{dF_o}{dE_K} \right) d^3K \\ &= \sigma T \left(\frac{k^2 \pi^2}{3e^2} \right). \end{aligned} \quad (6)$$

Because the integrals in the expressions for the electrical and thermal conductivity are the same, any anomaly in the electrical resistance from elastic scattering will also appear in λ .

The lattice thermal resistivity also consists of two major parts for $T < \theta/30$. It can be written

$$\begin{aligned} \frac{1}{\lambda_g} &= W_g = W_E + W_D \\ &= \frac{1}{bT^2} \quad , \end{aligned} \quad (7)$$

where W_E is the resistivity due to scattering of phonons by electrons and W_D is the resistivity due to scattering of phonons by dislocations. For well-annealed pure silver ($W_D \ll W_E$) $b = 2.0 \times 10^{-3}$ watts/deg³cm according to White, Woods and Elford (1959). From the results available it seems that $1/b$ does vary linearly with residual resistivity from an added impurity. According to White and Tainsh (1962) $1/b$ increases by about 30 to 35% over the value of pure silver when the residual resistance of the alloy is 1.0μ ohm cm.

Any conduction electron scattering process which involves an inelastic collision (electron energy not conserved) will generally affect the thermal resistivity and the electrical resistivity in different ways. Electrical resistivity depends on momentum scattering of electrons while the electronic thermal resistivity depends on both momentum and energy scattering. If the electron scattering is through a large angle and approximately elastic, the net effect will be to return the Fermi distribution to the equilibrium state that it occupies when there is no electric field or temperature gradient. Electrical and thermal resistivities

are then affected to almost the same extent. Also when the electron scattering is through a small angle and is elastic the electrical and thermal resistivities are affected in the same manner and the Wiedemann-Franz law holds. However, when the scattering is through a small angle and is inelastic, the thermal resistivity is the more drastically affected. When an electron loses energy of the order of kT it will change from a "hot" electron to a "cold" electron (relative to the Fermi surface) while the small angle scattering will only slightly change the direction of motion of the electron. From this viewpoint the thermal conductivity should indicate the presence or absence of inelastic scattering processes at low temperatures.

Yosida (1957), Kasuya (1959) and others indicate that there can be an exchange interaction between adjacent magnetic ions via the conduction electrons. If this is the case, any ferromagnetic (or antiferromagnetic) alignment of magnetic ions should be accompanied by inelastic scattering processes. That is, an electron may undergo a spin-flip when scattered by a magnetic ion. In the process it will lose an energy $kT \approx 1/2 \mu g H_i$, where μ is the Bohr magneton, g is the spectroscopic splitting factor, and H_i is an effective internal field. The individual ions experience a force which can be represented by a hypothetical

Weiss magnetic field H_1 . H_1 is a crude measure of the strength of the exchange interaction but gives no further information about the details of the exchange force.

I.4 Thermoelectric Power

The thermoelectric power of a specimen is given by measuring the voltage produced by a temperature gradient

$$S = \frac{\Delta V}{\Delta T} .$$

In the free electron approximation the presence of a thermal gradient will produce a voltage gradient simply because the "hot" electrons tend to diffuse more rapidly than the "cold" electrons, leaving the cold end negative with respect to the hot end of the sample. Assuming a constant relaxation time (e.g. scattering by non-magnetic impurities) and Fermi-Dirac statistics for the electrons one obtains

$$\begin{aligned} S &= \frac{\pi^2 k^2 T}{2eE_F} \\ &= \frac{C_{el}}{e} \text{ (neg) } , \end{aligned} \tag{8}$$

where e is the electronic charge (negative), E_F is the Fermi energy and C_{el} is the electron specific heat.

This is indeed true for pure sodium and potassium which have nearly spherical Fermi surfaces and, possibly rather surprisingly, is moderately well obeyed for the transition metals. The fact that Cu, Ag and Au have positive thermoelectric powers may be due to a considerable distortion of the Fermi surface.

If the electrons are not free, then the absolute thermoelectric power of a metal due to electron diffusion is (Wilson (1953))

$$\begin{aligned}
 S &= \frac{\pi^2 k^2 T}{3e} \left(\frac{d \ln \sigma(E)}{dE} \right)_{E=E_F} \\
 &= \frac{\pi^2 k^2 T}{3e} \left(\frac{d \log n(E)}{dE} + \frac{d \log v^2(E)}{dE} + \frac{d \log \tau(E)}{dE} \right)_{E=E_F}
 \end{aligned}
 \tag{9}$$

where $\tau(E)$ is the relaxation time, $n(E)$ is the density of electron states, and $v(E)$ is the velocity of an electron of energy E . This expression is expected to hold where

non-magnetic scattering is dominant, that is in the residual resistance region. For free electrons $n(E) \propto E^{\frac{1}{2}}$, $v^2 \propto E$, and $\tau \propto E^0$ so equation (8) follows.

It does not seem likely that the addition of an impurity should cause the first two terms in equation (9) to suddenly become very large (see MacDonald (1962)). It is therefore useful to notice the effect of an energy dependence in $\tau(E)$. Referring to the expression for the conductivity (4, 6) one can see that if $\partial F_0 / \partial E$ is symmetric about $E = E_F$, then only even terms in $\tau(E)$ contribute to the integral. On the other hand, in equation (9) only an odd term in $\tau(E)$ will contribute to the thermoelectric power. Guénault and MacDonald (1961) have analysed the effect of a highly energy dependent relaxation time τ . They found a large thermoelectric power is expected when τ is asymmetrical about $E = E_F$. In other words, "hot" and "cold" electrons have different scattering cross-sections. A large thermoelectric power is then indicative of an energy dependent scattering mechanism.

According to equation (8) the thermoelectric power S at low temperatures should be of the order of 10^{-8} volts/deg and vary linearly with temperature. However trace amounts of magnetic impurities in the noble metals produce thermoelectric powers which are larger than

10^{-6} volts/deg and are not proportional to temperature. This anomalous thermoelectric power seems to be associated with unusual low temperature variations of the electrical resistivity. For example see MacDonald (1962) and MacDonald, Pearson, and Templeton (1962).

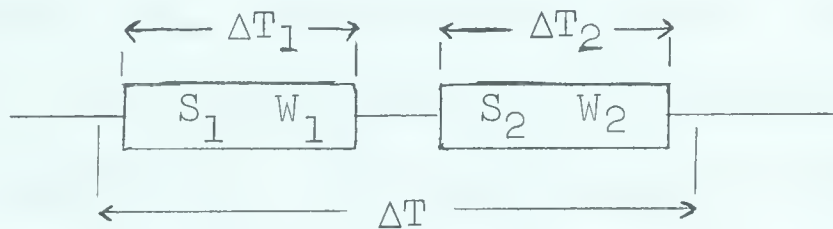
A second contribution to the thermoelectric power arises from phonon drag resulting from electron-phonon collisions. Electron-phonon processes can be of two types:

1. the Normal (N) processes in which the electron and phonon momentum is conserved. The phonons by collisions with electrons tend to sweep along the electrons, leading to a negative contribution to the thermoelectric power;
2. the Umklapp (U) processes in which the electron and phonon momentum is not conserved. Here an electron at the Fermi surface absorbs a phonon and thereby arrives at the Brillouin zone boundary. Now the electron can undergo a Bragg reflection, reversing its momentum leading to a positive contribution to the thermoelectric power.

The relative importance of N and U processes depends among other things on the shape of the Fermi surface, the distance of the Fermi surface from the Brillouin zone boundary and the temperature. The detailed analysis is

rather complex (Ziman (1960)) but in any event, the effects of the U processes dominate in the noble metals since they all have a positive hump at about $T \approx \theta/5$ in their thermoelectric power.

When the thermoelectric power results from several contributions, the component parts are not additive. Consider the case with two conductors connected in series with thermoelectric powers S_1 and S_2 and thermal resistances W_1 and W_2 respectively.



$$\begin{aligned} \text{The voltage difference} \quad \Delta v &= S_1 \Delta T_1 + S_2 \Delta T_2 \\ &= \left(S_1 \frac{W_1}{W_1 + W_2} + S_2 \frac{W_2}{W_1 + W_2} \right) \Delta T \end{aligned}$$

$$\text{Or in general} \quad S = \frac{\sum_i W_i S_i}{\sum_i W_i} \quad (10)$$

This can apply to a single conductor with various scattering mechanisms when one assumes that:

1. the scattering probability does not depend explicitly on the electron wave vector $\vec{K}$.

2. each electron collision is independent of preceding and succeeding collisions.
3. W_i is the electronic thermal resistivity.

Contributions from phonon drag and electron diffusion or anomalous electron scattering may be added to obtain the total thermoelectric power

$$S = S_e + S_g , \quad (11)$$

where S_e is the electron thermoelectric power and S_g is the phonon drag thermoelectric power. Since the latter term S_g is characteristic of the pure metal, S_e is easily separated. The thermoelectric power for pure silver has been measured by Pearson (1960).

I.5 Theories on Dilute Magnetic Alloys

A theory describing the anomalous thermoelectric power in dilute magnetic alloys must also describe the resistance minimum (and maximum) in a consistent fashion and vice-versa. A brief outline of the various models or explanations that have been used to explain these two anomalous effects is given below.

The first model, introduced by Korringa and Gerritsen (1953), supposes the existence of a highly

energy dependent scattering of electrons at the Fermi surface. They postulate that the addition of a magnetic impurity produces an energy level within $\pm kT$ of the Fermi surface. This energy level must be only partially filled to give energy dependent scattering. By developing this idea in terms of the free electron approximation Korringa and Gerritsen obtain a resistance minimum with a maximum at a lower temperature. A large thermoelectric power is also expected. The major objections to the above model are the difficulty in making an energy level extend throughout the lattice with very dilute alloys and the improbability of having an energy level within 10^{-4} electron volts of a Fermi surface (which is ~ 10 eV) for all the different concentrations of all different alloys in which a resistance minimum is observed. It should be noted that Korringa and Gerritsen encounter considerable difficulty in incorporating localized energy levels into the one electron theory of metals.

In the Brailsford-Overhauser model (1960) the magnetic ions are postulated to be either ferromagnetically or antiferromagnetically coupled in pairs. A scattering center (a pair of magnetic ions) is independent of similar scattering centers. This model gives a resistance minimum at the temperature where the coupling changes from

ferromagnetic to antiferromagnetic but it does not give a large thermoelectric power.

Kasuya (1959), de Vroomen and Potters (1961), and Bailyn (1961) have advanced a model in which the individual magnetic ions are coupled by a long range interaction. The spins of the ions are presumably coupled by means of the conduction electrons (Yosida (1957)). The effect of this long range interaction is replaced by a pseudo-Weiss field H_1 in order to make calculations. The conduction electrons are now divided into two groups - plus and minus spins - with respect to H_1 . If the scattering cross-sections for + and - spin electrons are different, and if there is inelastic scattering (spin-flips) then a large thermoelectric power is to be expected (Guénault and MacDonald (1961)). Kasuya, de Vroomen and Potters, and Bailyn follow through the model in detail and predict large thermoelectric powers at low temperatures. The sign of the thermoelectric power S depends on the sign of the interaction integral J for the conduction electrons and the d electrons of the magnetic ion. If J is positive (favoring antiparallel alignment of electron spin and magnetic ion spin), then S is negative. This model however predicts a monotonic decrease in resistivity with decreasing temperature. There is no likelihood of a resistance minimum without introducing some other mechanism.

In a model advanced by Kondo (1964a) he considers the second Born approximation in the scattering of conduction electrons by magnetic impurities. The magnetic impurity ions are supposed to be in a disordered state so the resistance minimum arises from the independent contributions of the ions. Calculating the expression for scattering to the second Born approximation and assuming the interaction integral J to be negative Kondo obtains a term proportional to $-c \log T$ in the resistivity, thus producing a resistance minimum. In a subsequent paper Kondo (1964b) obtains a large negative temperature independent thermoelectric power at low temperatures. Localized impurity spin terms can be dealt with when the scattering term is calculated to the second Born approximation. This latest theory may be viewed as a return to the original Korringa-Gerritsen idea.

PART II - APPARATUS AND PROCEDURE

II.1 The Cryostat

The cryostat used for this work has been described previously in some detail by Adler (1961) and Rogers (1962). Only a brief description will be given here.

The cryostat, which is shown in Figure 2 enables the measurement of the electrical and thermal resistivities and the thermoelectric power on the same specimen in the temperature range 2° to 100°K . This temperature range is broken into the following segments:

1. 2° to 4.1°K . The temperature is controlled by pumping on the liquid helium in the inner chamber to achieve pressures between one atmosphere and approximately 1 mm. of mercury.
2. 4.1° to 50°K . With the inner chamber evacuated the temperature is controlled by the electronic temperature controller (Dauphinee and Woods (1955)).
3. 55° to 90°K . With liquid oxygen instead of liquid helium around the outer can, the temperature is controlled by pumping on the liquid oxygen in the inner chamber.
4. Above 90°K . With liquid oxygen around the outer can

Helium
pumping
line

Vacuum
pumping
tubes

Liquid
air

Liquid
helium

s/c
reversing
switch
Glass-
metal
seal

Needle valve

Helium chamber

Outer can

Inner can

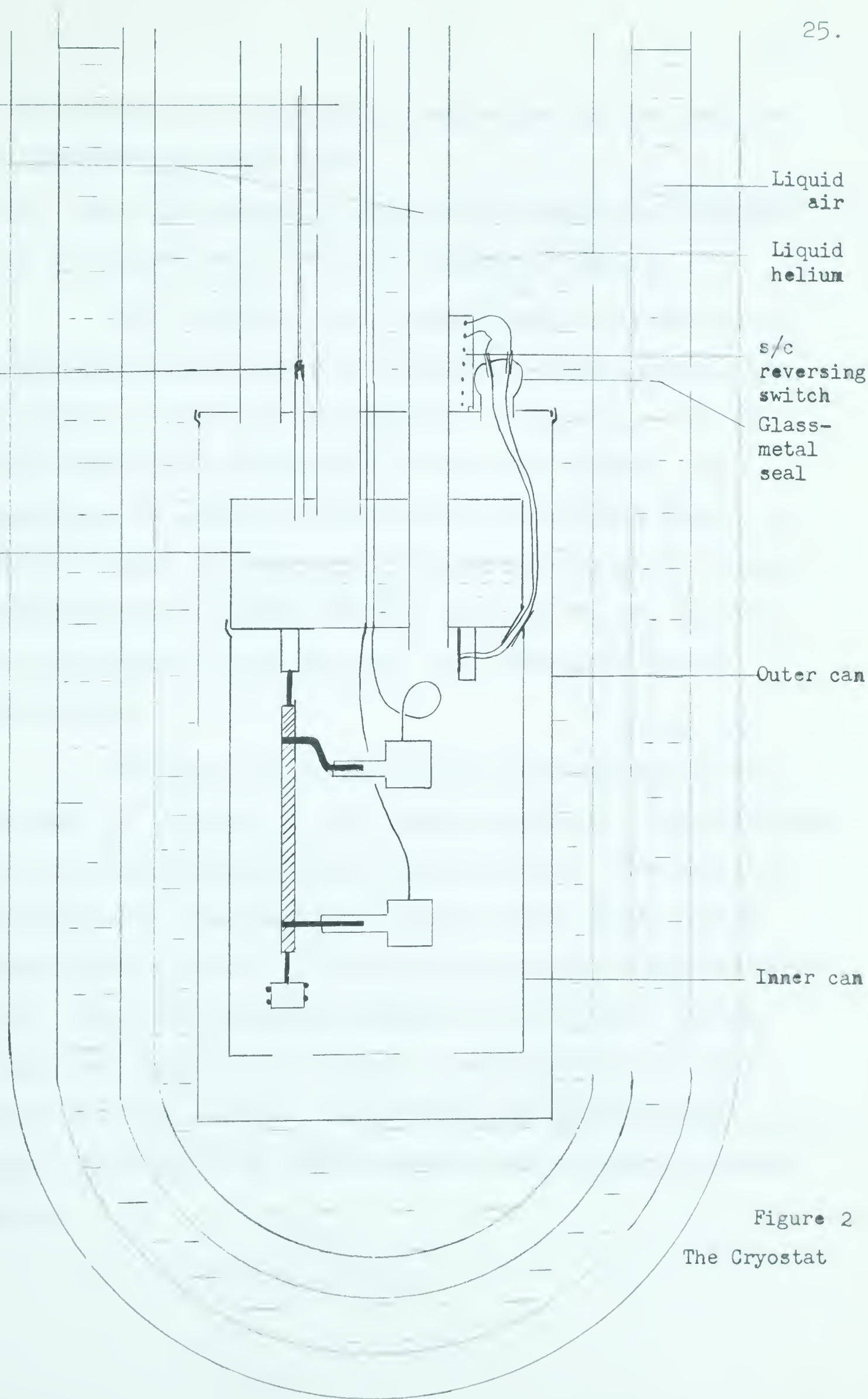


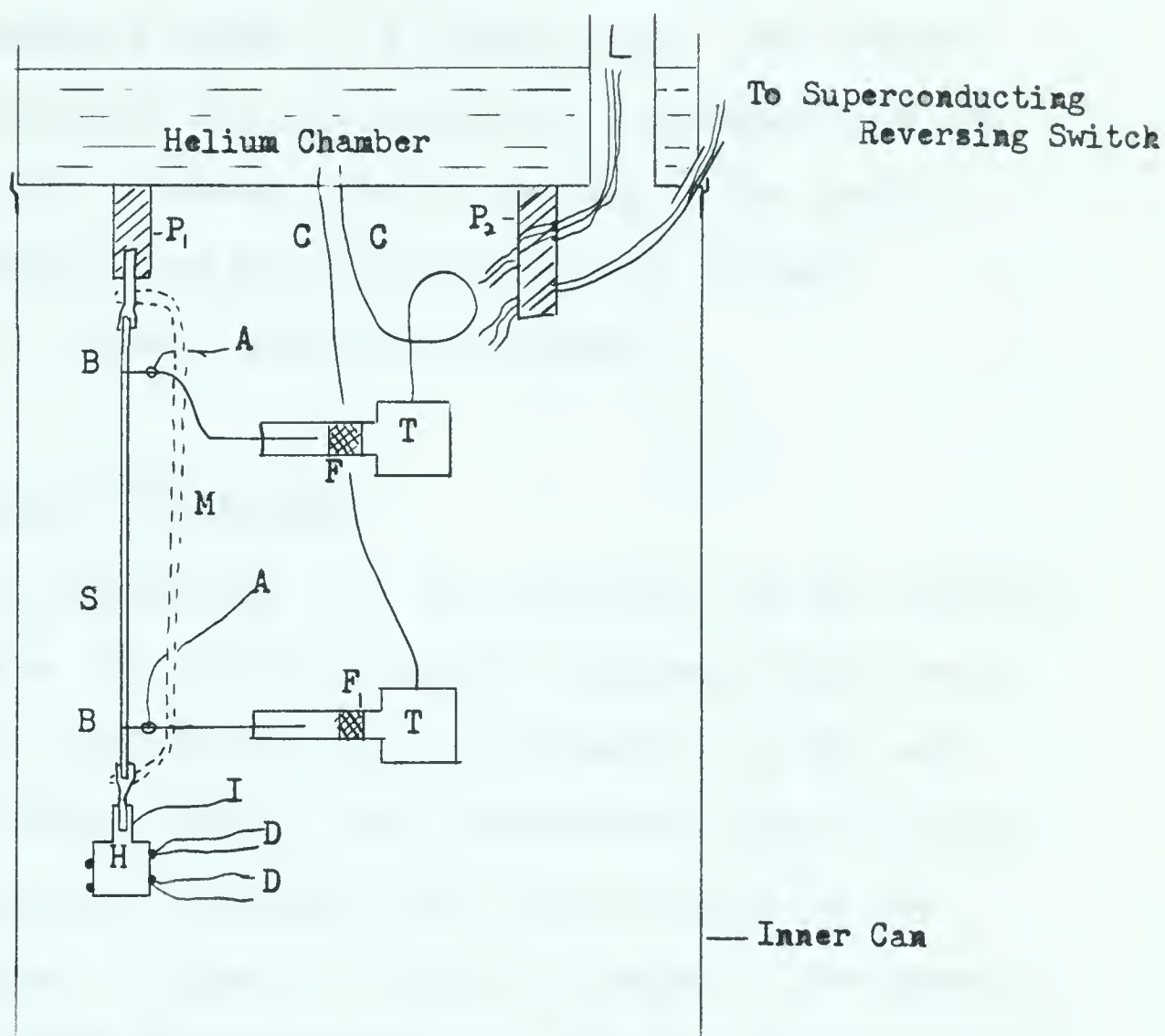
Figure 2
The Cryostat

the electronic temperature controller can be used for temperatures above 90°K .

At all times the sample is in a vacuum where the pressure is of the order of 10^{-5} mm. of mercury or lower.

The electrical and thermal resistivities and the thermoelectric power were all measured potentiometrically. The sample is shown in some detail in figure 3. One end of the specimen is attached to the inner chamber, the temperature of which is controlled as mentioned above. A specimen heater is attached to the other end of the sample to produce the necessary thermal gradient in the specimen. The connections to the specimen were made with Wood's metal solder.

Voltages and temperatures were measured at the same pair of contacts so the specimen geometry was eliminated from the determination of the Lorenz ratio. The potential contacts were soldered to the sample with Bi-Cd alloy solder which does not go superconducting above approximately 0.8°K . This was necessary to avoid an effective change in specimen length for electrical measurements due to a superconducting solder. In addition the poor thermal contact provided by a superconductor was avoided at these points.



- P_1 - Copper specimen mount
- P_2 - Isothermal copper post
- T - Gas thermometer bulbs
- A - Potential leads
- C - Capillary leads
- S - Specimen
- M - Glass specimen mount (if required)
- B - Bismuth-cadmium solder
- H - Heater
- I - Current lead
- D - Current and potential leads for heater
- F - Thermally conducting but electrically insulated junctions
- L - Electrical leads

Figure 3

The Specimen Chamber

The heater consists of manganin wire of about 400 ohms resistance wound on a copper form. The heater wire is electrically but not thermally insulated from the copper form with urethane plastic varnish. The heater power is obtained from measurements of the voltage across and the current through the heater.

II.2 Temperature Measurement

The temperature T of the specimen and the temperature difference ΔT produced by the specimen heater were measured with a differential gas thermometer in the way described by White (1959). The thermometer bulbs of about 5 cm^3 in volume were soldered with Wood's metal to the potential leads. A layer of cigarette paper in the arms of the bulbs isolates them electrically but not thermally from the sample. The bulbs are connected by german silver capillary tubes to a butyl phthalate manometer. Because the capillary tubes have an extremely high thermal resistance and the thermometer bulbs are gold plated to reduce radiation losses, the total heat loss is negligible.

The upper bulb is operated as a constant volume helium gas thermometer. The temperature is then obtained by applying the ideal gas law to the system. The expressions obtained for the temperature T , given by White (1959), is

$$T = P \left(\frac{T_0}{P_0} \right) \left(\frac{1 + \Delta}{1 + \Delta_0} \right),$$

where P is the pressure in the thermometer when it is at the unknown temperature T and P_0 is the pressure to which it was filled at the calibration temperature T_0 . $\left(\frac{1 + \Delta}{1 + \Delta_0} \right)$ is the factor that allows for the volume of the gas thermometer (capillary tubes) that is at room temperature.

The lower thermometer bulb is first filled to the same pressure as the upper bulb at T_0 and then is isolated from it. One manometer measures the pressure in the upper thermometer and another measures the pressure difference ΔP that appears between the two thermometers when the specimen heater is turned on. Each of these quantities is measured with a better accuracy than one percent. The temperature difference ΔT is given by

$$\Delta T = \Delta P \left(\frac{T_0}{P_0} \right) \frac{(1 + \Delta)^2}{1 + \Delta_0},$$

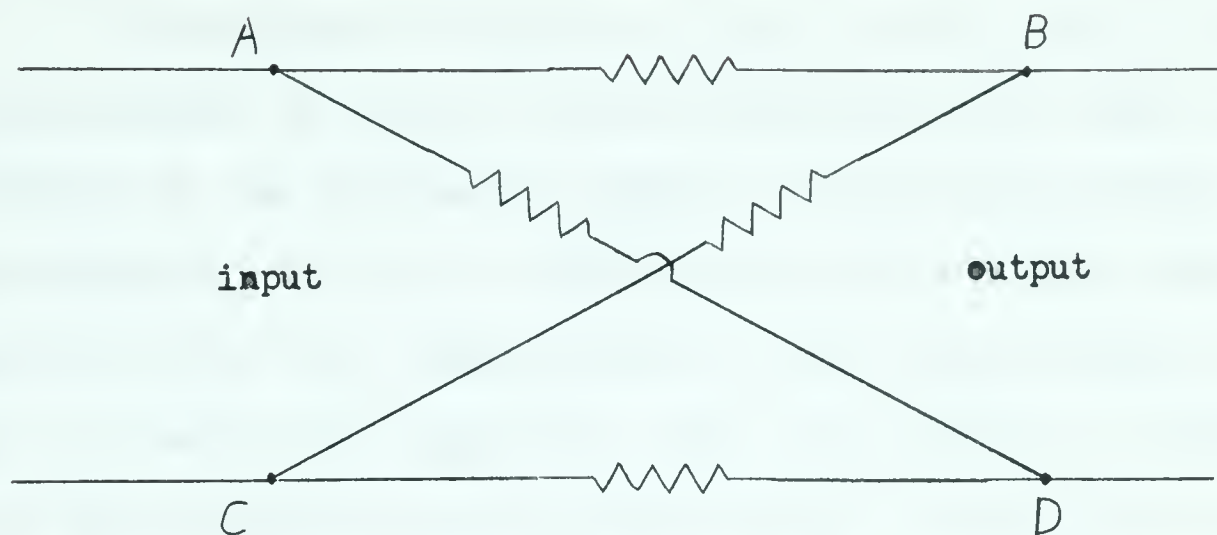
where $(1 + \Delta)^2 / (1 + \Delta_0)$ allows for the volume of the gas thermometer at room temperature. Graphs of $\frac{1 + \Delta}{1 + \Delta_0}$ and $\frac{(1 + \Delta)^2}{1 + \Delta_0}$ are given by MacFarlane (1963).

Once equilibrium is reached the temperature difference ΔT can be determined with an accuracy of one percent or better, depending on the calibration temperature.

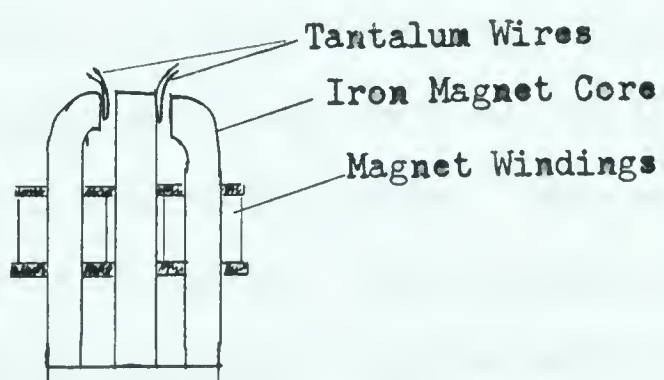
II.3 Voltage Measurement

To determine the resistance and the thermoelectric power the voltage difference between the potential terminals must be found. For electrical resistance measurements thin copper wires could be connected from a voltmeter at room temperature through one of the pumping tubes to the potential leads on the specimen. Before going to the specimen all wires coming into the specimen chamber from a high (ie. room) temperature region must be thermally anchored at the cryostat bath temperature and again at the inner chamber temperature so that practically none of the heat conducted by the electrical leads reaches the specimen. This thermal anchoring is done by wrapping several turns of the wire around copper posts, one of which is labelled P_2 in figure 3. However, thermal voltages in the wires leading to room temperature are frequently larger than the thermoelectric voltage arising from the specimen. Therefore it is necessary to include a reversing switch at liquid helium temperatures. Templeton (1955) has described a reversing switch that will operate satisfactorily in liquid helium.

Thin copper wires from the specimen potential terminals are first thermally anchored to post P_2 on the inner chamber and then brought out through a glass metal seal on the outer can to the superconducting reversing



Schematic Diagram



SUPERCONDUCTING REVERSING SWITCH

Figure 4

switch which is shown schematically in figure 4.

Referring to figure 4, AB, AD, BC, and CD are tantalum wires of several ohms resistance which pass between the poles of two different magnets. Tantalum becomes superconducting at only 4.4°K and thus has a low critical field at 4.2°K , the temperature of the liquid helium in which the switch is immersed. When one magnet is energized two of the tantalum wires become normal, leaving the other wires superconducting. For instance magnet 'a' drives AB and CD normal leaving A directly connected to D and C to B. Magnet 'b' drives AD and CB normal. Of course the source of the voltage must have a resistance much less than that of the non-superconducting tantalum wires, but our specimens have a resistance of less than 10^{-3} ohms compared with several ohms for the normal tantalum wires.

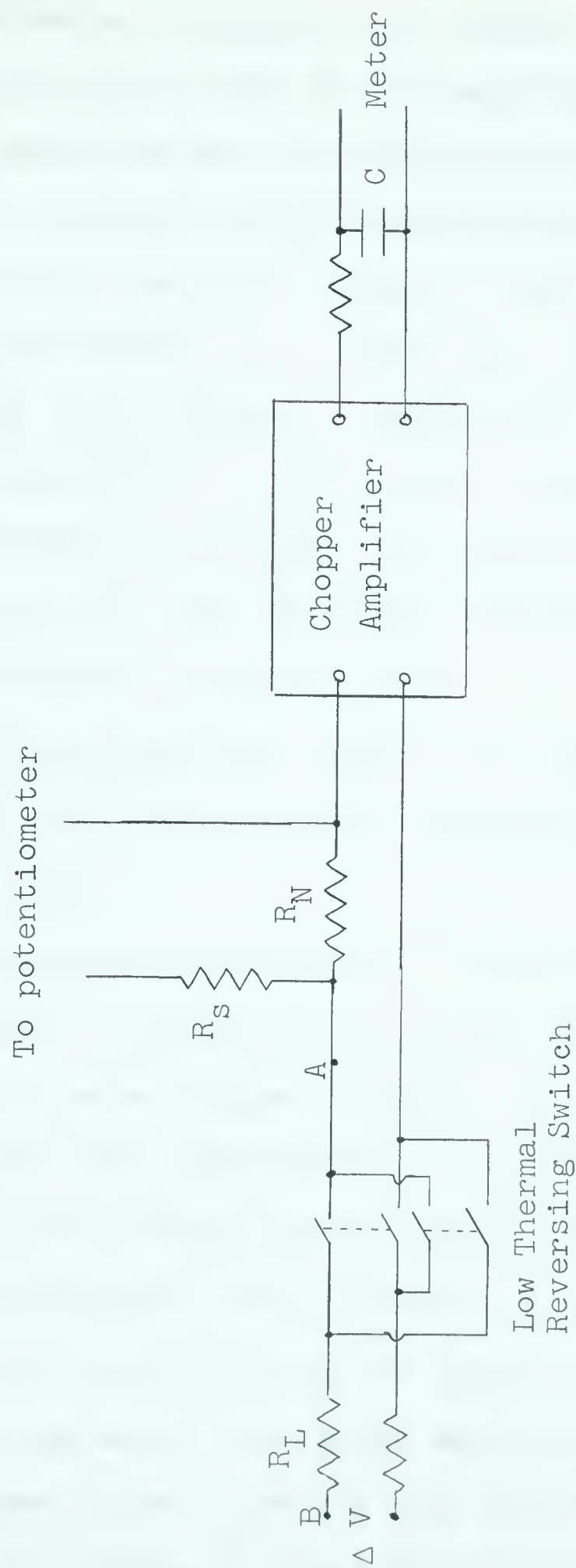
Three different voltage measuring devices were used. Since the voltages measured were as small as 10^{-8} volts, special techniques were required. The sensitivity had to be a few times 10^{-9} volts. Two systems involved chopper amplifiers while the other system was a galvanometer amplifier.

A. Chopper Amplifiers

The block diagram of both chopper systems is shown in figure 5. The small D.C. input voltage is formed

into a square wave with a set of low thermal choppers made by Guildline Instruments Ltd. The chopper speed was about 40 cycles per second (c.p.s.). The square wave from the choppers was amplified and then demodulated with a second set of choppers running in phase with the first. The output signal was connected to a filter network and a meter. A Cambridge potentiometer, adapted as a voltage source by shorting the galvanometer terminals, gave a voltage of opposite polarity to the input voltage so that the chopper amplifier system was used as a null detector. The size of the input voltage could then be read directly from the potentiometer dial. Because of the low voltages involved, the voltage at the potentiometer EMF terminals (shown on the potentiometer dial) was reduced by a factor of about 100 by a simple voltage divider. By means of calibration with standard resistors, the voltage across a neutral resistance R_N (specially wound to be thermal free) was found to be 0.9103×10^{-2} times the voltage indicated by the Cambridge potentiometer.

1. Originally a standard tube amplifier (Dauphinee and Woods 1955) was used to amplify the chopped D.C. signal. The smallest signal that could be detected above the noise with this system was 2×10^{-8} volts. In addition to 60 c.p.s. pickup in the input circuit



R_L - lead resistance

R_N - neutral resistor

$C = 160\mu\text{F}$ non-polarizable polystyrene capacitor

Figure 5

Block Diagram of the Chopper Amplifier System

there was an irregular noise signal that originated from the first stage of the amplifier. As a result this amplifier was not entirely adequate for the measurements. Another major problem occurred in choosing a ground for the input circuit. Both the potentiometer and the resistor R_S picked up a non-negligible amount of a 60 c.p.s. signal. Ideally the circuit should have been grounded at A, the neutral resistor, but in all measurements the sample was grounded at B, the cryostat. In effect the best grounding arrangement could be found only by trial and error.

This system was used in the experiments with the 0.067 and 0.063 atomic percent manganese alloys and the lead (Pb) wire.

2. The transistor equivalent of the tube amplifier designed by Soonpaa, et al (1963) was built because they quoted a noise figure of about 4×10^{-9} volts. This amplifier was independent of the power mains as it had its own battery power supply. Additional freedom in grounding was thus obtained.

This amplifier was at least as good as the tube equivalent and with a few minor design improvements would likely become better than the tube equivalent. However the 60 c.p.s. pickup of the input circuit was still substantial and not easily eliminated.

B. Galvanometer Amplifier

The galvanometer amplifier system described by Rogers (1962) and MacDonald (1947) was used in the remainder of the experiments to measure the small voltages.

A modification was made in the circuit to eliminate the need to use a potentiometer for calibration purposes. The voltage across a previously calibrated resistor of value $1000 \pm 3 \mu$ ohms was measured with the galvanometer amplifier. The current was measured with the same meter used for specimen currents, thus partially eliminating any systematic error from the meter.

Calibrated in this fashion the sensitivity of the galvanometer amplifier was found to drift less than 0.2% during an experiment when the most sensitive range ($R_F = 10$ ohms) was being used.

The galvanometer amplifier has an advantage over the chopper amplifiers because its response time is too large to be affected by 60 c.p.s. pickup. The smallest detectable voltage is about 5×10^{-9} volts. The device seems to be limited principally by building vibration and seismic noise.

Of the three devices the galvanometer amplifier is in my opinion the simplest and the most reliable.

II.4 Specimen Preparation

The abbreviations Ag and Mn will be used for silver and manganese respectively and the notation 'at. % Mn' or simply '% Mn' will be used in place of atomic percent manganese for convenience in referring to specific alloys.

Several alloys of manganese and silver were made in which the concentrations of manganese were less than 0.5 atomic percent manganese (at. % Mn).

The purity of the constituents was as follows:

Silver	Ag	a) 99.999% Pure, 59 grade, Lot HPM 4249 Cominco
		b) 99.9999+ % Pure, 69 grade, Lot HPM 2780 Cominco
		- used for samples with less than 0.05
		atomic percent manganese (at. % Mn).

Manganese	Mn	99.95% Pure; broken cathode manganese from
		Johnson, Matthey and Mallory.

The alloys were made using the radio frequency (R.F.) induction furnace in the Department of Mining and Metallurgy. The melting apparatus is shown in figure 6. A small hole was made in the alumina crucible (99.7% pure recrystallized alumina). The crucible with the alumina stopper and pieces of metal in place was placed in a heating coil. The entire assembly was surrounded by a bell jar.

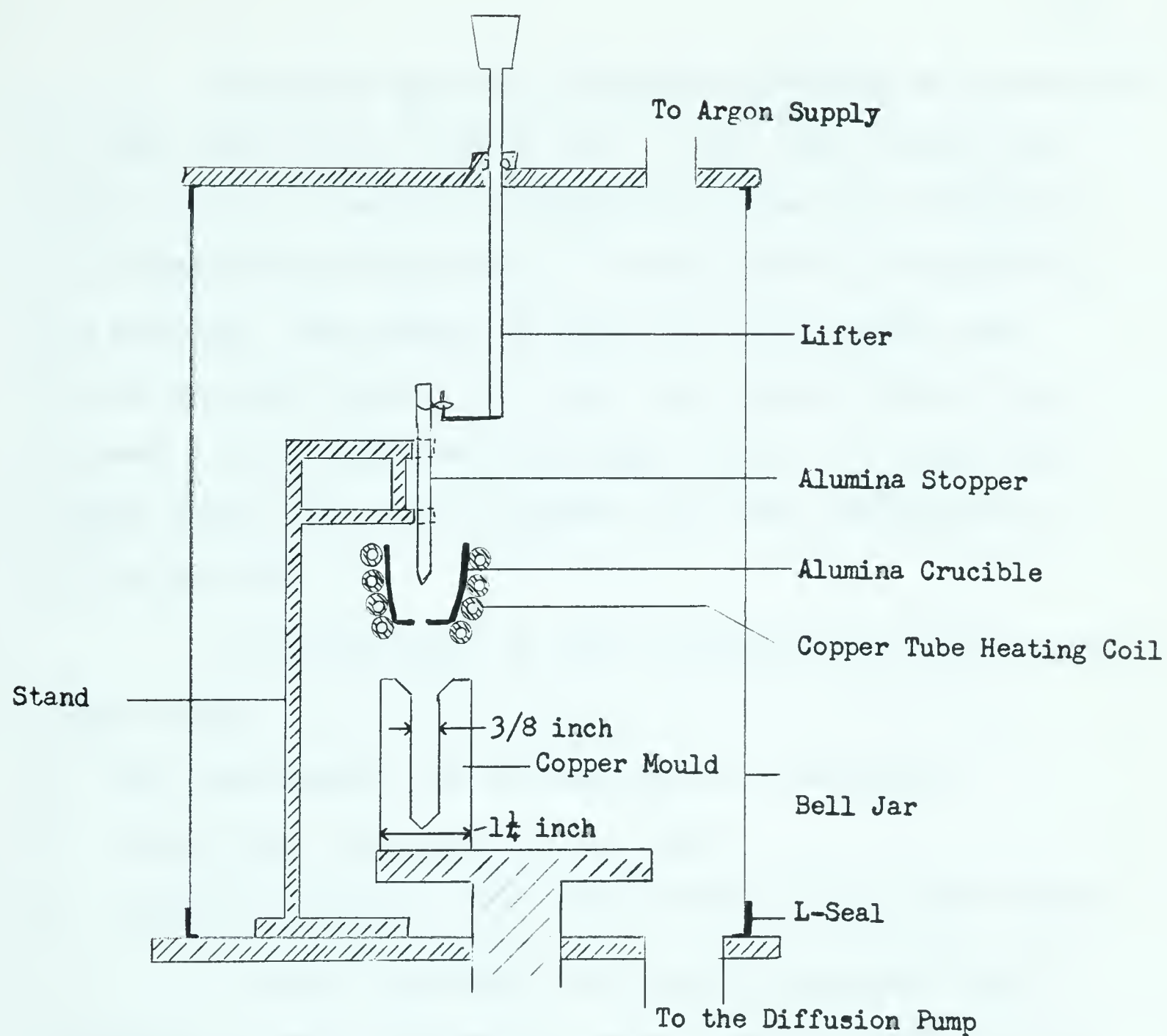


Figure 6

Induction Furnace Melting Assembly

The bell jar was initially evacuated to a pressure of less than 5×10^{-4} mm of Hg. It was then filled with argon gas at a pressure slightly less than one atmosphere to minimize the evaporation of either the Mn or Ag during the melting. The pieces of metal in the crucible were melted and kept molten for about one minute before being allowed to run into the cold copper mould. A large cold copper mould was used to prevent any phase separation of the Ag and Mn.

The advantages of this technique for melting are three fold:

1. The environment for melting may be controlled.
2. Chance for contamination is small.
3. Complete mixing of the constituents in an alloy occurs.

Because we wanted very small concentrations of manganese it was necessary to make a master alloy of about 5 at. % Mn and to perform one or two successive dilutions of the master alloy.

At all stages care was taken to avoid introducing any spurious impurity to the samples. The silver and silver alloys were etched in 40% nitric acid and the manganese was etched in 5% hydrochloric acid.

The chill cast samples were rolled to a thickness of less than 1 mm. From the resulting sheet a rectangular

piece was cut with a carborundum saw. Depending on the dimensions of specimen required, this rectangular piece was used, or the sample was drawn into the form of a wire using diamond dies. After each of the above steps the sample was etched briefly to remove any contamination.

The specimens were then placed in quartz boats in the vacuum chamber of a resistance furnace. The vacuum chamber was subsequently evacuated to a pressure of less than 2×10^{-4} mm of Hg. The temperature was initially raised to 500°C until the vacuum chamber and specimens inside were outgassed and subsequently to 750°C for four hours.

To check on the effectiveness of the annealing process and also the purity of the silver, samples of 59 and 69 grade silver were rolled and then annealed in this way also. The residual resistivity, which varies with the impurity atom and dislocation density, was measured. The results are given below.

$$\begin{array}{l} \text{59 grade silver} \quad \frac{R_{4.1}}{R_{293}} = 1.1 \times 10^{-3} = \frac{1}{907} \\ \text{69 grade silver} \quad \frac{R_{4.1}}{R_{293}} = 9.7 \times 10^{-4} = \frac{1}{1030} \end{array}$$

Samples were made with the following nominal concentrations:

0.31 atomic percent manganese in silver (at. % Mn)

0.145 at. % Mn

0.067 at. % Mn

0.063 at. % Mn

0.025 at. % Mn

0.005 at. % Mn.

According to Gerritsen (1956) for dilute binary solid solutions the observed resistivity ρ can be written as

$$\rho = \rho_1 + \rho_b$$

where

$$\rho_b = c\delta\rho_2 + c^2\delta'\rho_3 .$$

The resistivity of the pure metal is represented by ρ_1 , and the impurity concentration in atomic percent by c .

The coefficient $\delta\rho_2$ is the resistivity increase per atomic percent of impurity. For manganese in silver $\delta\rho_2 = 1.60 \times 10^{-6}$ ohm cm/atomic percent manganese at 273°K and $\delta'\rho_3$ is neglected (see Gerritsen (1956)). Assuming Matthiessen's rule to be valid for very dilute binary solid solutions, then ρ_b is proportional to the concentration of manganese in silver.

<u>Nominal concentration in atomic percent manganese</u>	<u>Residual Resistivity</u>	<u>$\rho_b / (1.60 \times 10^{-6})$ in atomic percent</u>
0 (69 grade silver)	$.0016 \times 10^{-6}$ ohm cm	-
4.93 at. % Mn	$7.8 \pm 0.2 \times 10^{-6}$	4.9 at. % Mn
0.311	$0.510 \pm 0.005 \times 10^{-6}$	0.32
0.145 (A)	$0.173 \pm 0.005 \times 10^{-6}$	0.11
0.025 (B)	0.038×10^{-6}	0.024
0.0051	1.10×10^{-8}	
$\rho - \rho_1 \approx$	0.94×10^{-8}	0.0058

Two samples were sent to the Chicago Spectro Service Laboratory Inc. for analysis. The results are given below in weight percentages (wt %).

<u>Element</u>	<u>Sample A</u>	<u>Sample B</u>
Silver	99.86 weight percent	99.87 weight percent
Manganese	0.054 wt % = 0.104 at %	0.014 wt % = .027 at %
Aluminum (approx.)	< 0.001 wt %	0.06 wt %
Silicon (approx.)	0.01 wt %	0.01 wt %
Iron (approx.)	0.07 wt %	0.05 wt %
Copper (approx.)	0.006 wt %	0.0006 wt %

The silver percentage is obtained by difference, that is by subtracting the percentages of the impurities from one hundred percent. The analysts suggested that the relatively

large percentage of iron present was due to contamination from the sampling procedures. The residual resistance measurements given above do indeed indicate that there is no iron in solid solution.

The manganese percentages by analysis agree to about one part in ten or less with the manganese percentages deduced from residual resistance measurements. Furthermore the nominal manganese concentrations, in all but one case, agree to less than six parts per hundred with the manganese concentrations deduced from residual resistance measurements.

The results shown in the tables above indicate that a manganese concentration of 0.001 atomic percent might have been attained. However, great care must be exercised to avoid the introduction of spurious impurities to very dilute alloys.

II.5 Experimental Procedure

The room temperature resistance of the samples was measured after they were mounted in the cryostat. From this, a measurement of the residual resistance, and a knowledge of the room temperature resistivity of pure silver, an effective shape factor ℓ/A was calculated. (Shape factors from the known geometry of the specimens agree with the resistivity data to within $\pm 5\%$.)

The experimental chamber was cooled with liquid air. The gas thermometers were filled with helium gas at this temperature. A few measurements were made on some samples in the liquid air temperature range. For measurements at liquid helium temperatures the dewar arrangement was changed to that shown in figure 2 and the experimental chamber was then cooled with liquid helium.

The pressure in the experimental chamber for liquid helium experiments was less than 5×10^{-6} mm of Hg as indicated by a cold cathode Martin gauge at room temperature. Measurements were made in the range between 4 and 30°K and then the gas thermometers were refilled at the temperature of the liquid helium bath. Then measurements were made in the range between 2 and 8°K. Electrical resistivity measurements were made on the isothermal sample and then the heater was turned on to produce a temperature gradient in the sample. Then the temperature difference and the voltage difference between the potential leads (with no specimen current) was measured to give the thermal conductivity and thermoelectric power of the specimen.

PART III - RESULTS

We measured the electrical resistivity, thermal conductivity and thermoelectric power of the following alloys:

0.31 atomic percent manganese in silver
0.11 at. % Mn
0.067 at. % Mn
0.063 at. % Mn
0.005 at. % Mn
0 at. % Mn ("Pure" silver)

The silver measured had a residual resistivity ratio of about 1/500 and exhibited no anomalies in either the thermoelectric power or the electrical resistivity. For this reason we conclude that there was no manganese in solid solution in the silver.

The samples containing 0.067 at. % and 0.063 at. % Mn originated from different melts. The results are not substantially different, so the results for the 0.063 at. % Mn specimen have not been included.

The electrical resistivity was found to be consistent to within less than one-half percent while the thermal conductivity results fall within a ± 2 percent range. The thermoelectric power readings may be in error by about $\pm 2 \frac{1}{2}$ percent. These are maximum limits for error and usually the consistency is much better.

The results are shown in tabular form followed by graphs of the results.

III.1 Tables of Experimental Results

TABLE I

0.31 atomic percent manganese (at % Mn)

TEMPERATURE	ELECTRICAL RESISTIVITY	THERMAL CONDUCTIVITY	ABSOLUTE THERMO- ELECTRIC POWER
T	ρ	λ	S
1.35°K	0.484 μ OHM CM.		
1.84		0.098 $\frac{\text{WATTS}}{\text{DEG. CM.}}$	+0.51 $\frac{\mu\text{V}}{\text{DEG.}}$
1.88	.491		
1.97		.106	+ .38
2.03	.493		
2.08		.111	+ .31
2.52	.500		
2.56		.139	+ .02
3.01	.507		
3.025		.167	- .29
3.55		.204	- .51
3.60	.507		
4.13	.509		
4.205		.252	- .78
5.37	.511		
5.45		.352	-1.09
6.25	.513		
6.33		.433	-1.32
6.79	.512		
6.74		.475	-1.38
7.55	.509		
7.79		.803	-1.35
9.05	.510		
9.43		.737	-1.36
10.86	.509		
11.21		.860	-1.28
12.7	.508		
13.1		.998	-1.15
14.7	.508		
15.0		1.105	- .98
16.8	.509		
17.4		1.27	- .84
18.7	.510		
19.1		1.41	- .70
22.1	.516		
22.4		1.60	- .52
25.8	.524		
26.3		1.72	- .10

TABLE II

0.11 at % Mn in Ag

T	ρ	λ	S
1.24° K	0.1709 μ OHM CM.		
1.93	.1723		
2.01		0.308 $\frac{\text{WATTS}}{\text{DEG. CM.}}$	-1.01 $\frac{\mu V}{\text{DEG.}}$
2.07	.1726		
2.19		.341	-1.12
2.31	.1727		
2.40		.374	-1.25
2.69		.424	-1.39
2.71	.1731		
3.17	.1733		
3.29		.521	-1.57
3.64	.1730		
3.72		.593	-1.64
4.14	.1727		
4.22		.668	-1.68
6.19	.1716		
6.33		1.103	
6.82	.1710		
8.68	.1699		
10.20	.1689		
10.40		1.90	-1.76
12.7	.1685		
13.0		2.38	-1.57
15.5	.1690		
16.2		2.88	-1.31
18.7	.1710		
19.5		3.55	- .85
22.05	.1752		
22.7		3.66	- .44
24.8	.181		
25.4		4.05	- .18

TABLE III

48.

0.067 at % Mn in Ag

T	ρ	λ	S
1.90°K		0.537 $\frac{\text{WATTS}}{\text{DEG. CM.}}$	
1.91	0.0965 $\mu\text{OHM CM.}$		
2.03	.0966		
2.18		.577	-1.87 $\frac{\mu\text{V}}{\text{DEG.}}$
2.28	.0967		
2.60		.71	-1.7
2.78	.0961		
2.87		.802	
2.93	.0962		
3.05		.884	-1.90
3.205	.0955		
3.45	.0954		
3.55		1.015	-2.20
3.61	.0955		
3.67		1.093	
4.13	.0948		
4.21		1.23	
4.24		1.22	-2.31
5.58	.0941		
5.66		1.725	
6.16		1.81	
6.82		2.13	-2.42
6.91	.0937	2.07	
8.15	.0933		
8.20	.0934		
8.90		2.72	-2.27
9.70	.0931		
9.74		3.05	
9.77	.0930		
10.66		3.14	-2.19
11.9		3.50	-2.01
13.05	.0934		
14.6		4.34	-1.80
17.4	.0954		
17.6		5.02	-1.38
20.6		5.38	-.92
21.2	.1007		
21.6		5.31	
24.7		5.95	-.43
31.7	.129		
35.6	.145		

TABLE IV

0.005 at % Mn in Ag

T	ρ	λ	S
1.31° K			-2.2 $\frac{\mu V}{DEG.}$
1.39	1.162 x 10 ⁻⁸ OHM CM		
1.84	1.141		
1.95		4.92	-3.22
2.32	1.130		
2.38		5.75	-3.13
2.86	1.121		
2.94		7.13	-3.14
3.36	1.115		
3.45		8.20	-3.25
3.72	1.112		
3.82		9.20	-3.10
3.75	1.113		
4.12	1.111		
4.20		10.27	-3.14
4.83	1.107		
6.43	1.103		
6.55		16.32	-3.29
6.57		16.37	-3.19
6.58	1.102		
7.60	1.104		
7.83		19.03	-3.04
8.26	1.104		
8.27		19.3	-2.78
9.12	1.105		
9.31		21.3	-2.73
11.28	1.116		
11.61		25.1	-2.44
13.6	1.159		
13.9		26.5	-1.96
15.9	1.25		
16.4		26.2	-1.35
20.9		23.9	- .37

TABLE V

O at % Mn in Ag ("Pure" silver)

T	ρ	λ	S
1.27°K	0 .663 x 10 ⁻⁸ OHM CM		
1.72	.662		
1.98	.663		
2.26	.664		
2.59	.664		
2.67		9.89 $\frac{\text{WATTS}}{\text{DEG. CM.}}$	+0.01 $\frac{\mu\text{V}}{\text{DEG.}}$
3.29		12.00	+ .02
3.64	.664		
3.74		14.01	+ .03
4.14	.664		
4.25		15.85	+ .05
5.24	.666		
5.4			+ .18
6.04	.671		
6.62			+ .23
7.06	.676		
7.25			+ .37
8.34	.690		
8.51			+ .39
10.29	.719		
10.33			+ .59
12.9	.800		
13.0			+ .82
16.2	1.014		
16.5			+1.13

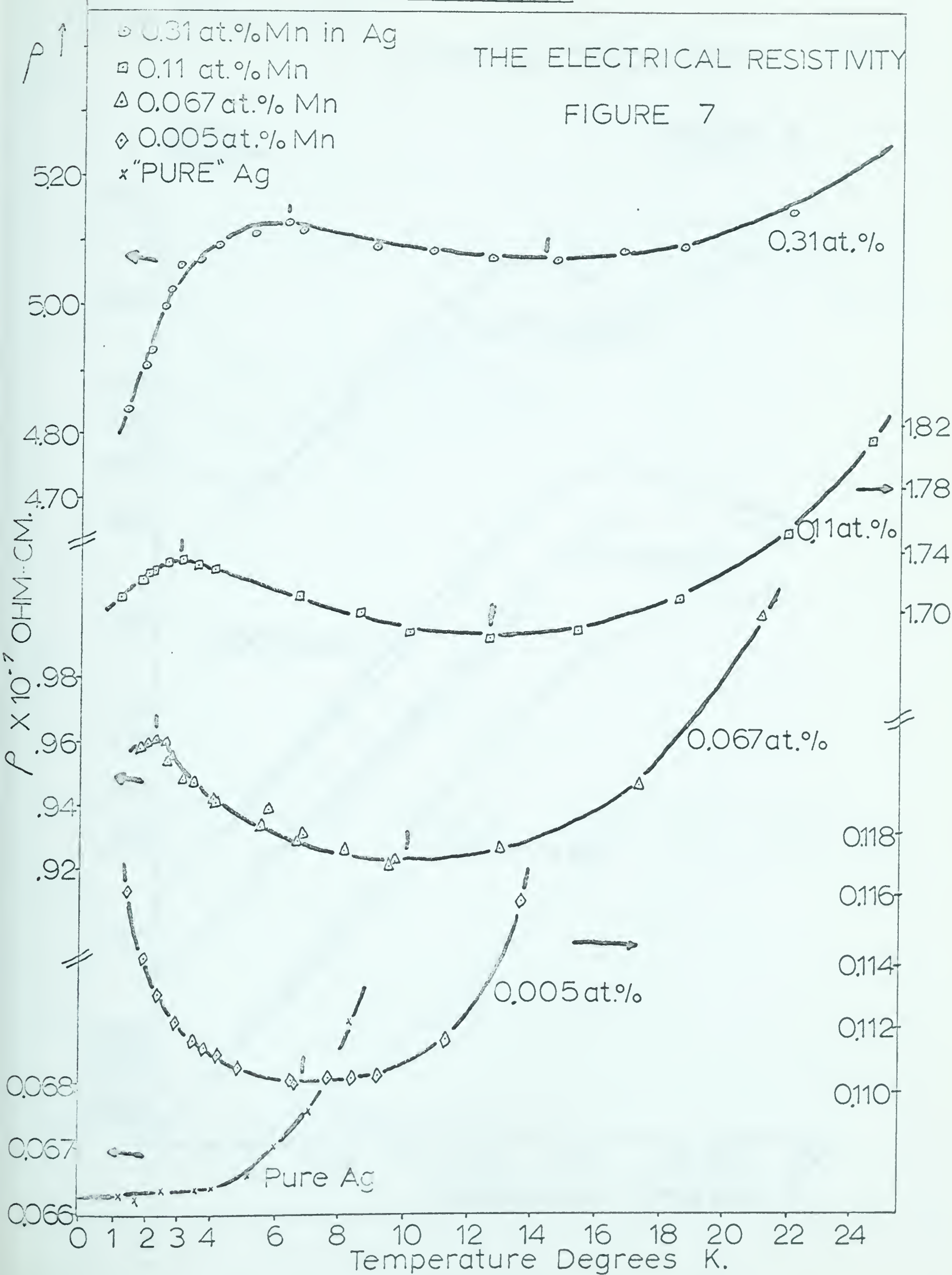
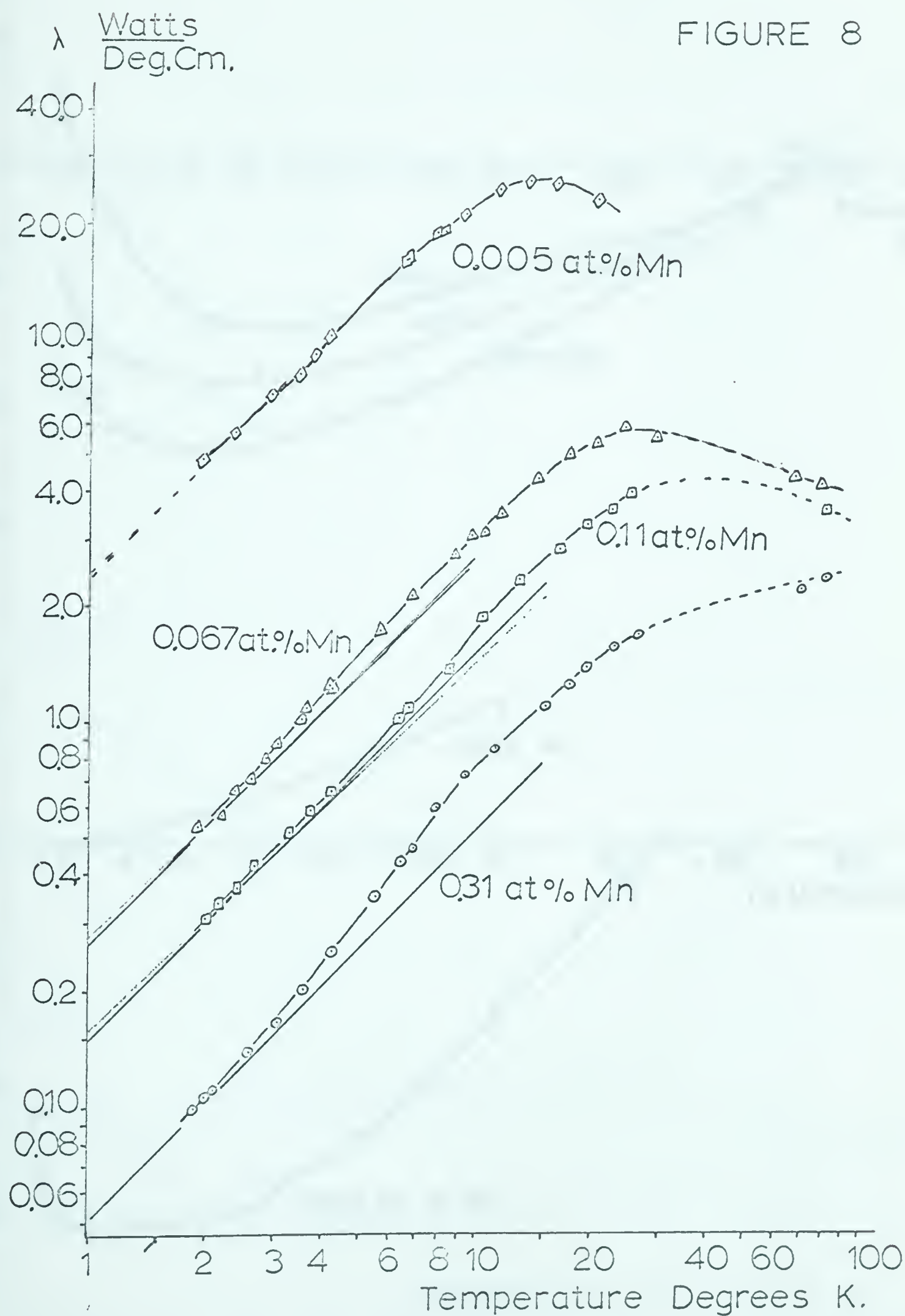


FIGURE 8



THERMOELECTRIC POWER

53.

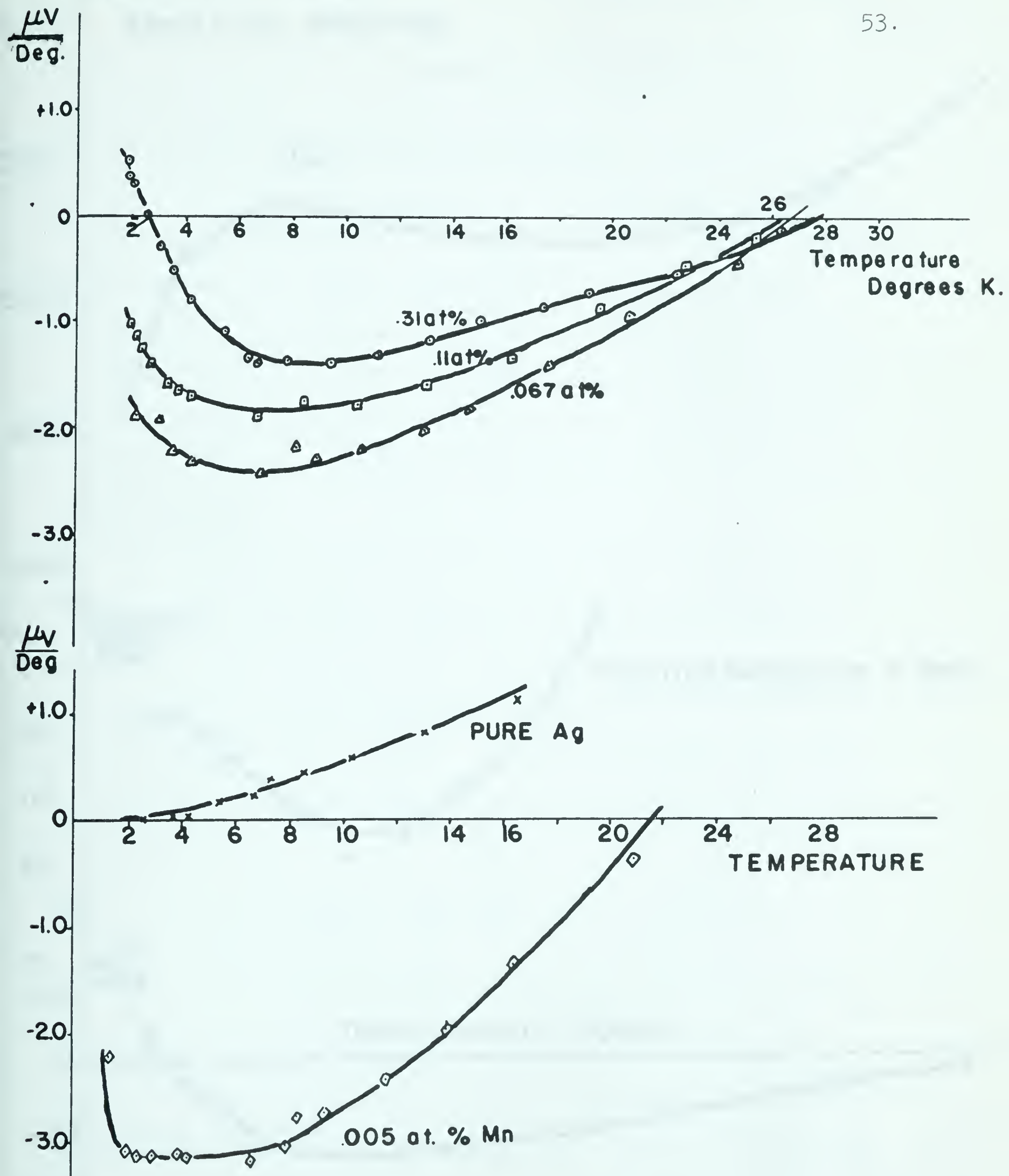


FIGURE 9

$\rho - \mu \text{ OHM-CM.}$

.31at.%Mn. in Ag.

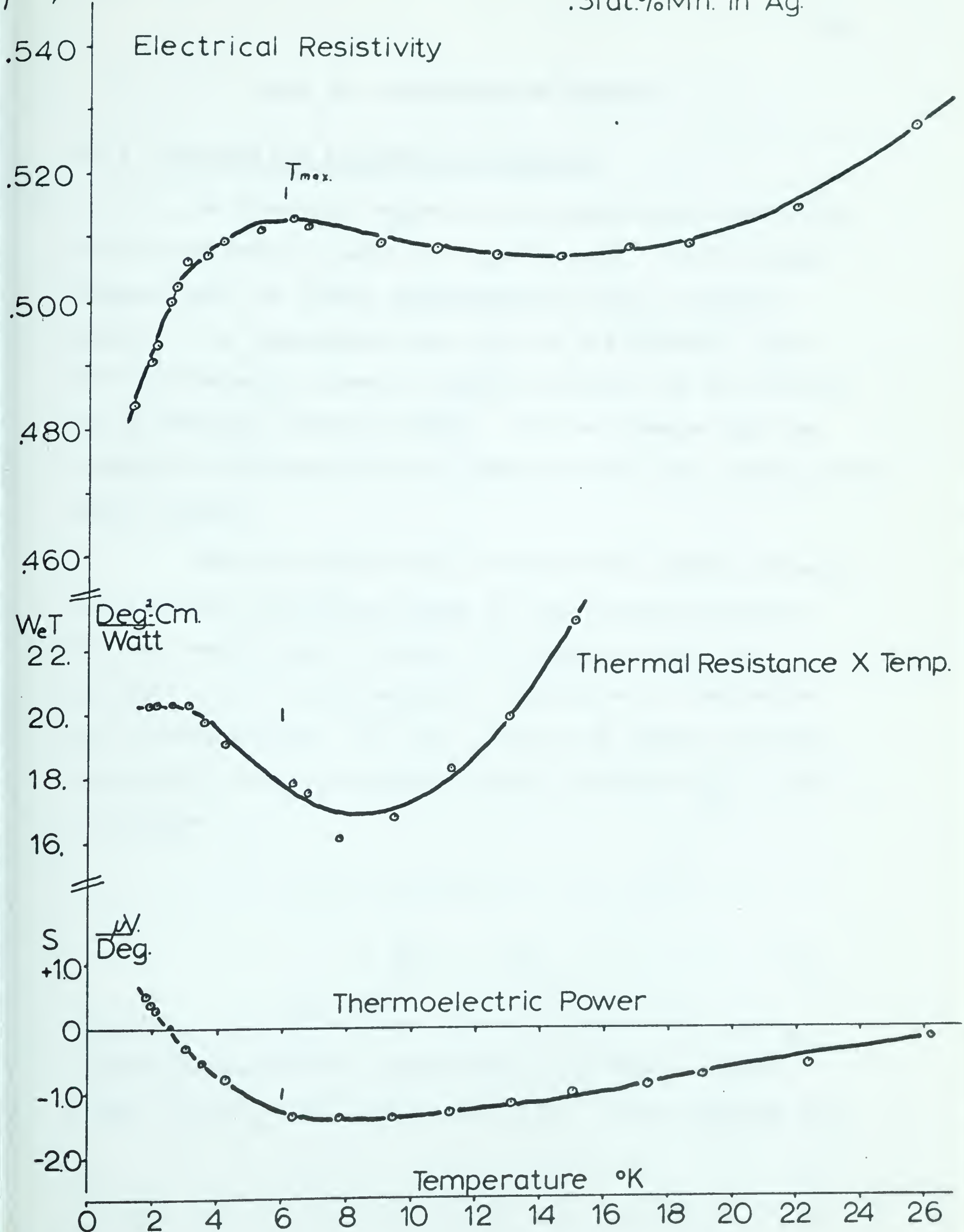


FIGURE 10

PART IV - DISCUSSION OF RESULTS

IV.1 Analysis and Discussion of Results

We observed a minimum in the electrical resistivity in all the samples except the "pure" silver. In the three samples with the larger concentrations of Mn, a maximum appears at a temperature below that of the minimum. Also the thermoelectric power is negative whereas for pure silver it is positive (Pearson (1960)). It thus appears that the anomaly in the resistivity is associated with the thermoelectric power anomaly.

Analysis of the thermal conductivity results presents considerable difficulty because of their unusual behavior. For most metals and for dilute non-magnetic alloys the quotient λ/T varies reasonably linearly with temperature at low temperatures. If, for a moment, we ignore the ideal resistivity term, the measured thermal conductivity λ can be written

$$\begin{aligned}\lambda &= \lambda_e + \lambda_g \\ &= \frac{L_0 T}{\rho_0} + bT^2\end{aligned}\tag{5}$$

where λ_e is the electronic thermal conductivity and λ_g is the lattice thermal conductivity. For dilute alloys where $\lambda_e \gg \lambda_g$ the Lorenz ratio $\rho\lambda/T$ should approach the

Sommerfeld value $L_0 = 2.45 \times 10^{-8}$ watt ohm/deg² as $T \rightarrow 0$. Instead, the experimental values of the Lorenz ratio for all the alloys at a temperature where $\lambda_e \gg \lambda_g$ are somewhat larger than L_0 .

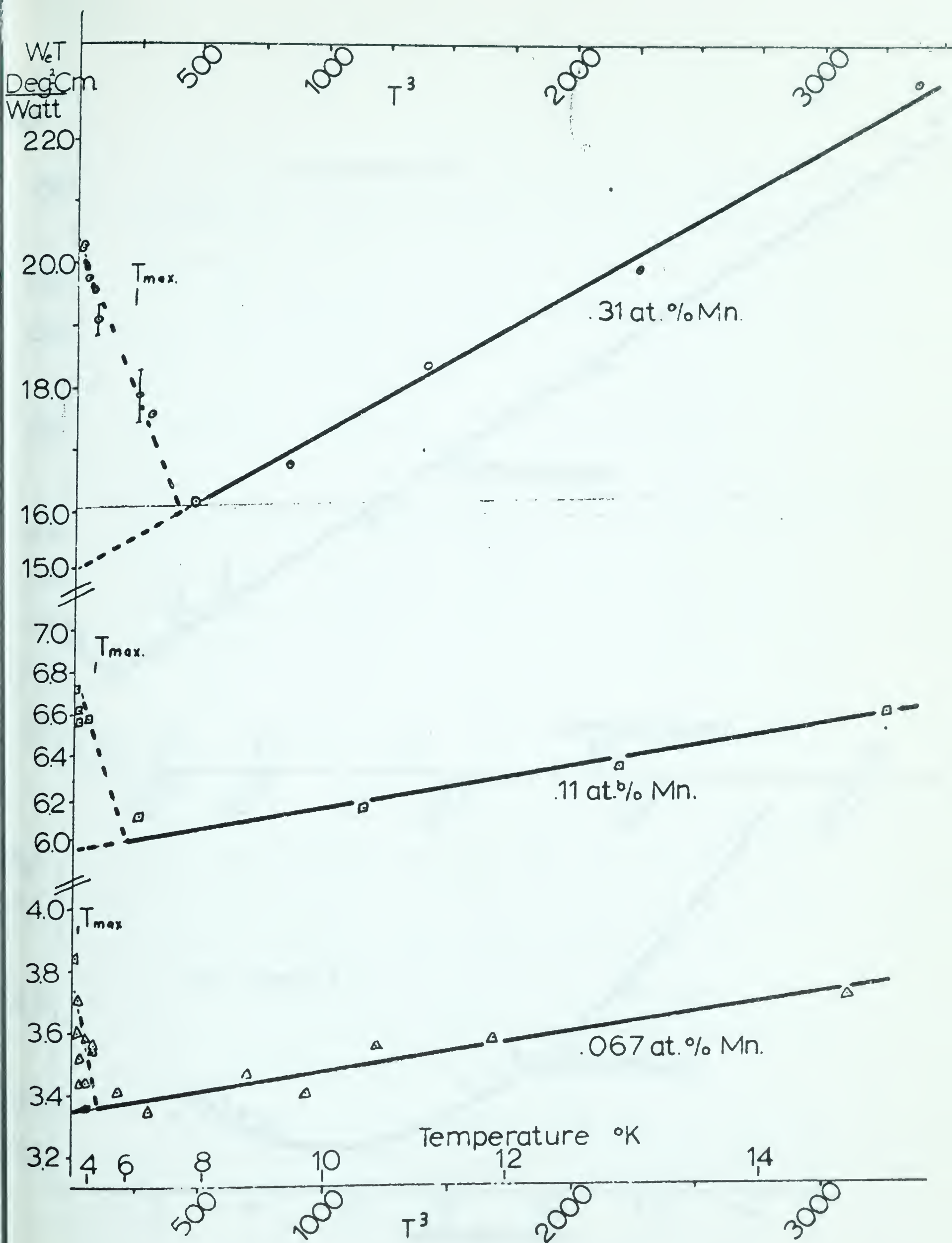
Alloy	Temperature	Experimental Lorenz number
0.067 at. % Mn	3.05°K	2.77×10^{-8} watt ohm/deg ²
0.11 at. % Mn	3.29	2.74
0.31 at. % Mn	3.02	2.82
0.005 at. % Mn	2.94	2.72
"Pure" Ag	3.29	2.44

Therefore one cannot calculate the electronic thermal conductivity at higher temperatures using the Wiedemann-Franz relationship.

In order to calculate the electronic thermal resistivity W_e without using the Wiedemann-Franz law, the lattice thermal conductivity was calculated to give $\lambda_e = \lambda - \lambda_g$. The electronic thermal conductivity for a normal metal can be written

$$\frac{1}{\lambda_e} = W_e = \frac{A}{T} + BT^2 \quad (5a)$$

so that the constants A and B can be determined from a plot of $W_e T$ versus T^3 .



$W_e T$ versus T^3

FIGURE 11

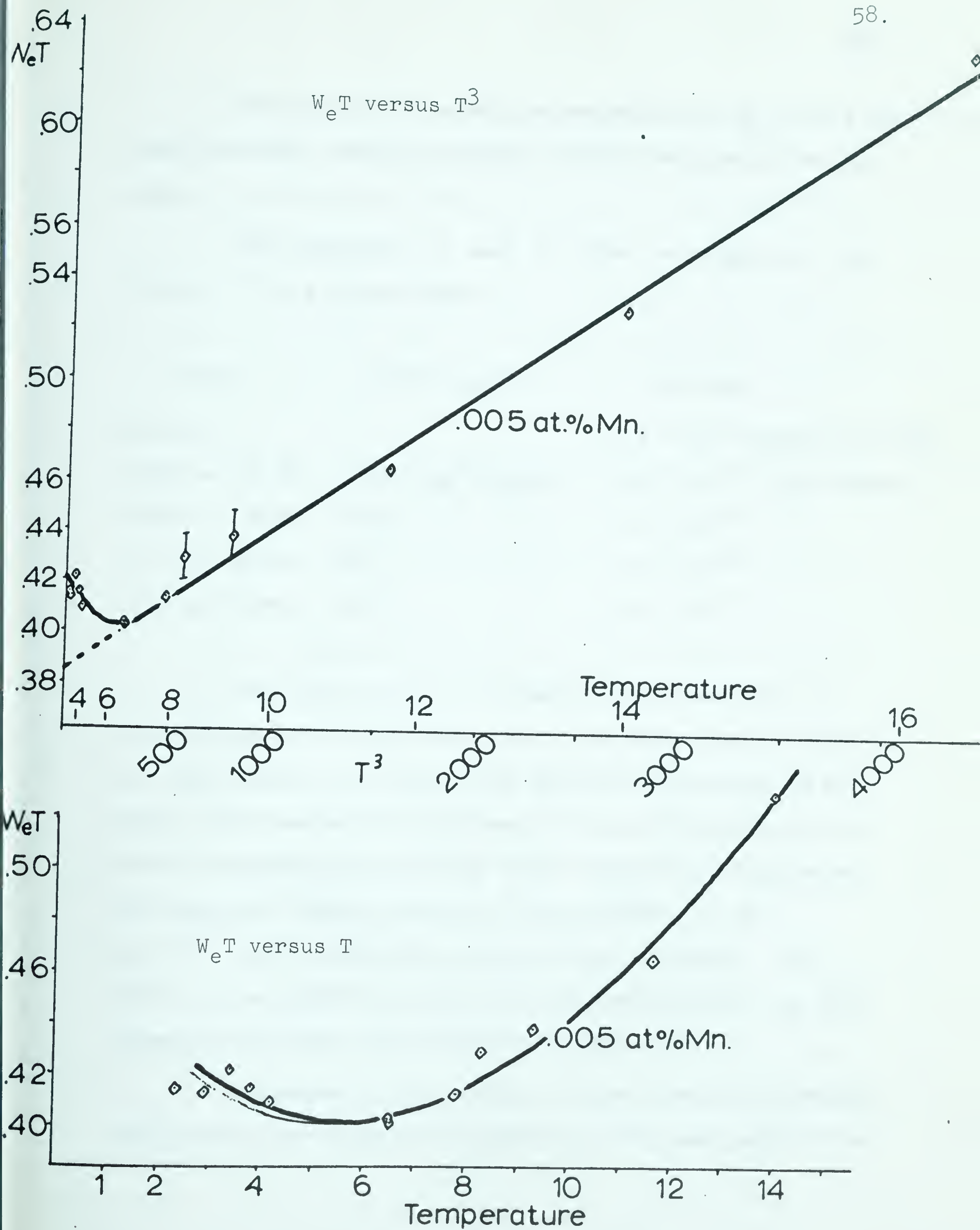


FIGURE 12

The value of the lattice resistivity $\lambda_g = 2.0 \times 10^{-3} T^2$ found by White, Woods and Elford (1959) for pure silver was used.

The constants A and B from the graphs of $W_e T$ versus T^3 are given below.

Alloy	A(intercept)	B(slope)
Pure Ag	-	0.5×10^{-4} Rosenberg(1955)
0.005 at. % Mn	0.385 Deg ² cm/watt.	0.55×10^{-4} Deg ⁻¹ cm/watt.
0.067 at. % Mn	3.35	1.1×10^{-4}
0.11 at. % Mn	6.0	1.9×10^{-4}
0.31 at. % Mn	15.0	23×10^{-4}

The value of B, a constant characteristic of electron-phonon interaction, should decrease from the value for pure silver by no more than 20% for the 0.31 at. % Mn alloy. The unexpected increase with impurity concentration in the experimental values of B can probably be eliminated by choosing a smaller value of the constant b in $\lambda_g = bT^2$ as the impurity concentration increases. The effect of an impurity on the lattice conductivity λ_g has already been noted and estimated on page 13.

A minimum in the product of the electronic thermal resistivity and temperature appears at the same temperature

as and is the same relative size as the electrical resistance minimum in the 0.005 at. % Mn alloy. This indicates that elastic electron scattering processes are responsible for the resistances.

The peculiarity in the $W_e T$ versus T^3 curves for the three alloys with the greatest amount of Mn present cannot be removed by any adjustment of λ_g . The minimum in the $W_e T$ versus T curves of these alloys does not come at the temperature of the resistance minimum, and the size of this minimum is many times larger than an effect corresponding to the resistance minimum. (See for example figure 10).

The Sommerfeld value L_0 of the Lorenz ratio is obtained when the values of ρ and WT for the 0.31 at. % and 0.11 at. % Mn alloys are extrapolated to absolute zero. This indicates that elastic processes are responsible for the resistances at absolute zero.

The departure of the $W_e T$ versus T^3 plots from the expected linearity at low temperatures is probably a result of inelastic electron scattering processes. Schmitt and Jacobs (1957) have studied the low temperature magnetic behavior of dilute manganese in copper alloys which exhibit resistive characteristics similar to those of our silver manganese alloys. They observed a cooperative magnetic

transition in their alloys. Without saying anything about the exchange interaction between individual ions, one can say that below the transition temperature the spin degeneracy of the magnetic ions is removed. Inelastic scattering involving spin-flips of the electron with respect to the ion can occur at low temperatures. This inelastic scattering will be quenched as the absolute zero of temperature is approached.

If two electron energy levels separated by an energy ΔE are present near the Fermi surface, then a decrease in the electrical resistance should begin at a temperature T given by $kT \sim \Delta E$. A maximum in the thermal resistivity temperature product $W_e T$ should appear at roughly $T \sim \Delta E/4k$ (see Ziman, p. 382 (1960)).

If a maximum in $W_e T$ due to inelastic scattering does occur, it is below the lowest temperature reached even for the alloy containing 0.31 at. % Mn. The thermal conductivity of an alloy of about 0.6 - 1.0 at. % Mn should reveal the existence of a maximum in $W_e T$.

A maximum in the thermoelectric power S occurs in the 0.31 at. % Mn alloy somewhere below the lowest temperature achieved (see figure 9) because S must approach zero as $T \rightarrow 0$. A positive contribution to the thermoelectric power first becomes noticeable at about the tempera-

ture $T_{\max}$ of the resistance maximum in both the 0.31 at. % Mn alloy (figure 10) and the 0.11 at. % Mn alloy.

We suggest that this positive term in S is due to the splitting of the electron energy levels by a cooperative magnetic interaction between the magnetic ions in solution. De Vroomen and Potters (1961) find a maximum in the absolute value of the thermoelectric power S at a temperature $T \sim \Delta E/3k$ in calculating the thermoelectric power resulting from a cooperative interaction between the magnetic ions in solution. They find that purely anti-ferromagnetic ordering will result in zero contribution to S for reasons of symmetry while purely ferromagnetic (parallel) ordering of the magnetic ions will result in a maximum contribution to S . On the basis of their magnetic susceptibility measurements Schmitt and Jacobs (1957) propose that dilute manganese alloys consist of small ferromagnetic domains coupled antiferromagnetically. De Vroomen and Potters state that the sign of the thermoelectric power which they calculate depends on the sign of the exchange integral J between the conduction electrons and magnetic ions. If J is positive (favoring anti-parallel alignment) then S is negative and vice-versa. Lacking any positive information from another source on the sign of J , we consider it here as an adjustable parameter. In this case, if J is

negative, then there is a positive thermoelectric power anomaly in the temperature region where there is some type of magnetic ordering. This positive value of S corresponds to that observed by us and also to that observed for manganese copper alloys by Kjekshus and Pearson (1962).

A detailed analysis of resistive and thermoelectric power anomalies resulting from two energy levels separated by a single value of ΔE is too simple minded. Rather a spectrum of energy separations should be used. The broadness of the specific heat anomaly which was observed by de Nobel and du Chatenier (1959) in dilute manganese silver alloys indicates that a spectrum of ordering temperatures exists. According to Marshall (1960) this spectrum is caused by the random separation of Mn ions in solution.

Chari and de Nobel (1959) have measured the thermal conductivity of some Ag Mn alloys in the liquid helium, liquid hydrogen and liquid nitrogen temperature ranges. They observed an unusual kink at about 2° or 3°K in the λ versus T curve of silver manganese alloys, a silver indium alloy and some steels. This kink has not been observed in any of our results. (Figure 8)

The temperature T_{max} of the resistivity maximum in our alloys was found to vary approximately linearly with the concentration of the manganese in the silver in agreement

with Gerritsen and Linde (1951).

The electrical resistance minimum and the resistance maximum appear to be two separate effects. A resistance minimum can occur without the presence of a maximum. The resistance of gold with 0.006 atomic percent iron measured to about 0.01°K by MacDonald, Pearson, and Templeton (1962) showed no resistance maximum whatsoever. On the other hand, the resistance of silver with two percent Mn measured by Gerritsen and Linde (1951) showed only a sharp decrease of resistance below some characteristic temperature. No resistance minimum was seen.

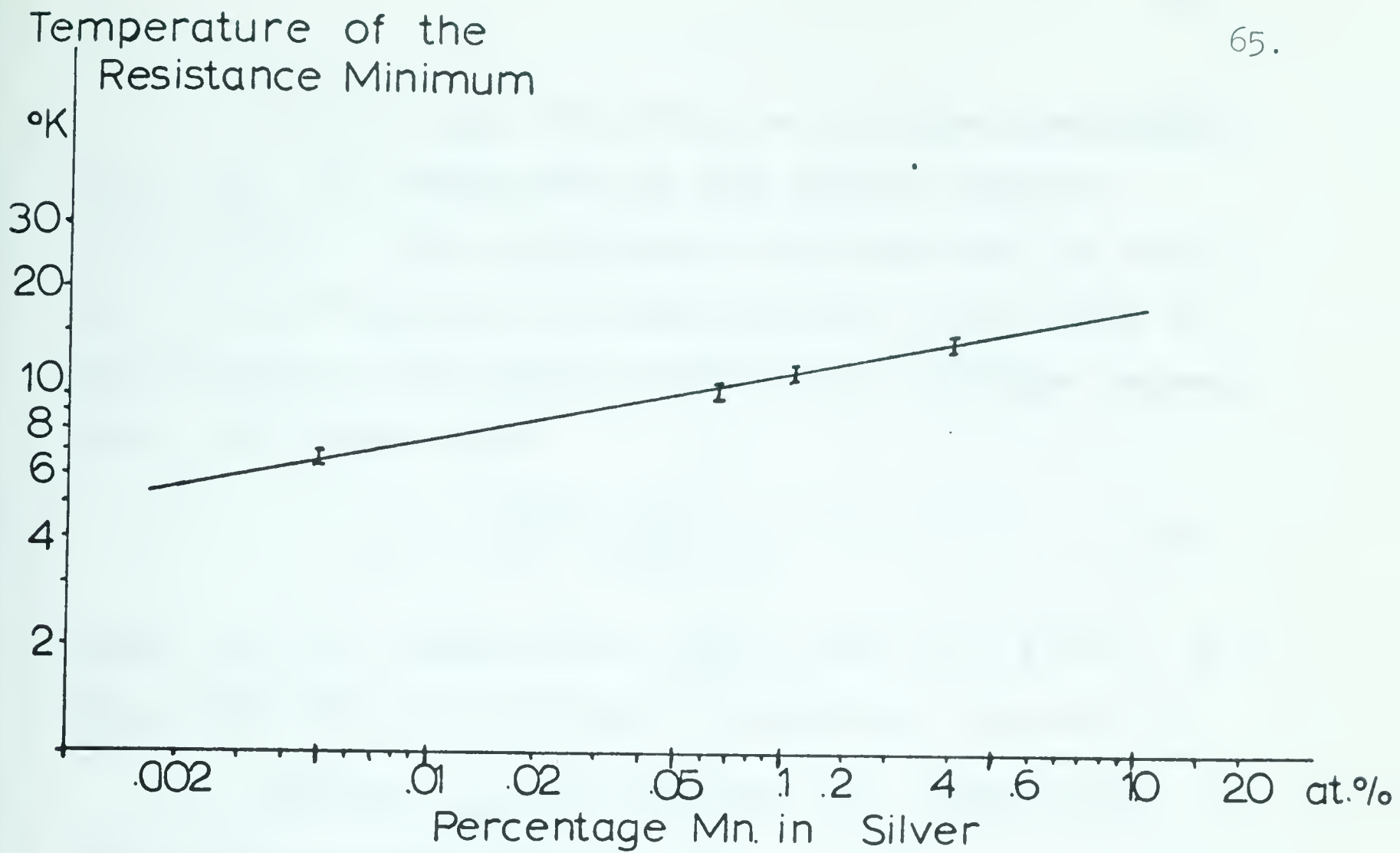
The temperature $T_{\min}$ of the minimum in the electrical resistance shows a much slower variation with manganese concentration than does $T_{\max}$. Figure 13 shows that $T_{\min} = 18.5 c^m$ with m falling in the range 1/5.0 to 1/5.5. Such a dependence would be expected if the anomalous term in the resistivity can be represented by $-cp' \log T$, where ρ' is a positive constant. Then, ignoring the maximum,

$$\rho = \rho_0 + c \rho_2 + aT^5 - cp' \log T. \quad (12)$$

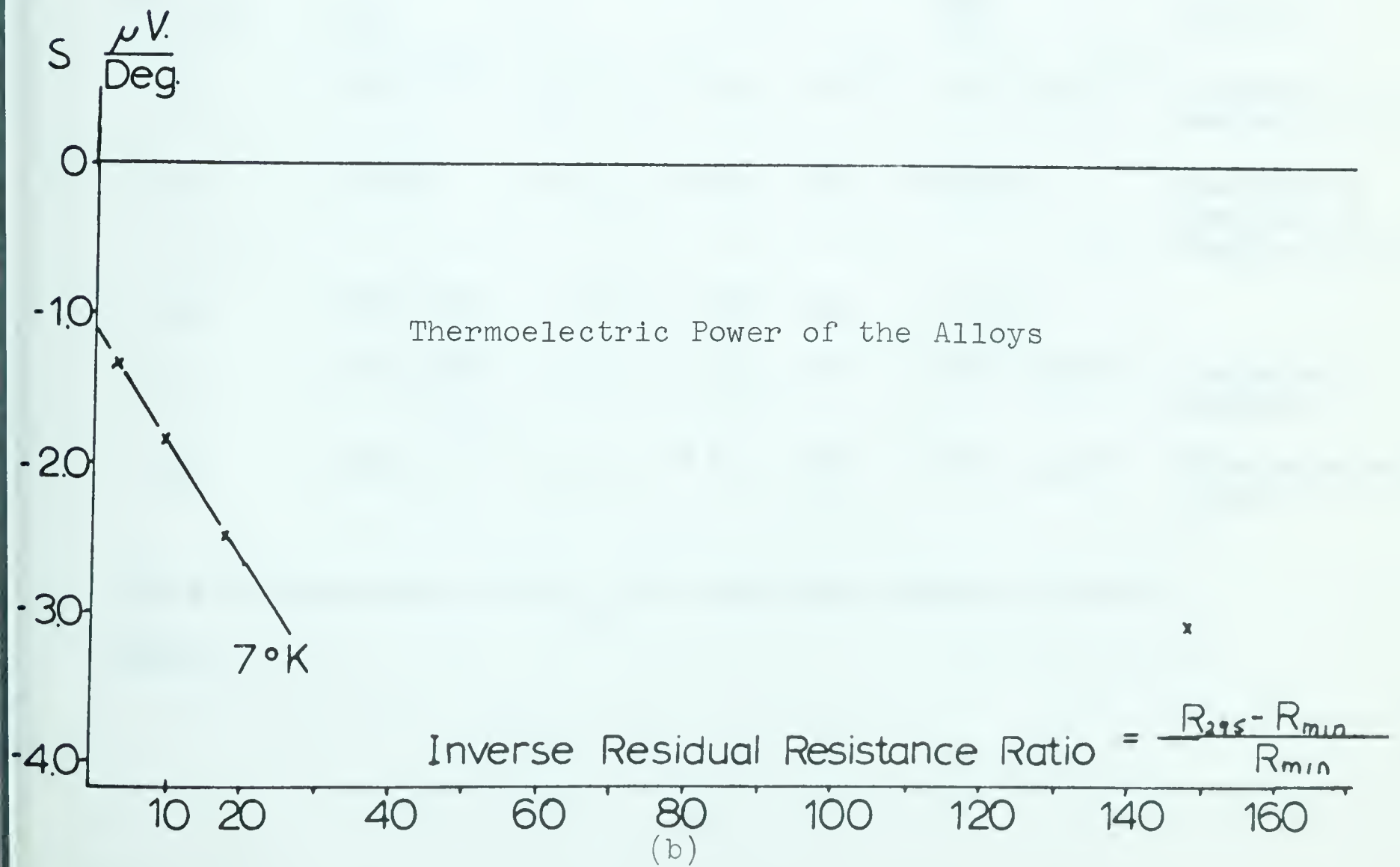
At the minimum

$$\frac{d\rho}{dT} = 0 = 5aT^4 - \frac{cp'}{T}$$

$$\text{so } T_{\min} = (cp'/5a)^{1/5} \quad (13)$$



(a)



(b)

Usually $T_{\min}$ for silver is at a lower temperature than $T_{\min}$ for copper with the same magnetic impurity concentration. This corresponds to the fact that the value of 'a' is much smaller for copper than for silver. This in turn depends on the relative sizes of θ , the Debye temperature. From Ziman (1960)

$$\rho_i = 4\left(\frac{T}{\theta}\right)^5 J_5\left(\frac{\theta}{T}\right) \rho_\theta \quad (14)$$

where ρ_θ is a constant and $J_5\left(\frac{\theta}{T}\right) \rightarrow 124.4$ as $T \rightarrow 0$. So $T_{\min} = K\theta$ where K is defined by equations (13) and (14).

Consider $T_{\min}$ for manganese in copper (Cu), silver (Ag), and gold (Au).

Solvent	$T_{\min}$	c	θ	$\frac{T_{\min}}{\theta}$	Source
Cu	$19 \pm 0.5^\circ\text{K}$	0.1 at. % Mn	340°K	$5.6 \pm 0.2 \times 10^{-2}$	Kjekshus & Pearson '62.
Au	$10 \pm 1^\circ\text{K}$	0.1 at. % Mn	165	6.0 ± 0.6	MacDonald, Pearson, & Templeton '61.
Ag	$12 \pm 0.5^\circ\text{K}$	0.1 at. % Mn	225	5.3 ± 0.2	
Cu	$15 \pm 0.5^\circ\text{K}$	0.03 at.% Mn	340	$4.4 \pm 0.2 \times 10^{-2}$	Kjekshus & Pearson
Ag	9.5 ± 0.5	0.03 at.% Mn	225	$4.2 \pm 0.2 \times 10^{-2}$	interpolated value.

There is agreement of $T_{\min}/\theta$ among the various solvent metals.

According to Kondo (1964a) the electrical resistivity of dilute magnetic alloys is given by

$$\rho = \rho_o + \rho_i + \rho_s \quad (3)$$

$$= aT^5 + \rho_1 + c\rho_A + c\rho_m + c\left(\frac{3zJ\rho_m}{E_F}\right) \log_e T \quad (15)$$

where ρ_A and ρ_m are constants characteristic of the solvent and solute, z is the number of free electrons per atom, and E_F is the Fermi energy (5.5 eV for silver). Then the "spin" resistivity ρ_s is given by

$$\rho_s = -c\rho' \log\left(\frac{T_1}{T_2}\right) = \rho(T_1) - \rho(T_2) - a(T_1^5 - T_2^5). \quad (16)$$

The ideal resistivity of silver likely obeys a T^5 law at low temperatures. White and Woods (1958) obtain an exponent of 4.7. Since there seems to be no published value for the coefficient a in $\rho_1 = aT^5$ for silver, it is deduced using equation (14) from the value for copper which is 2.6×10^{-16} ohm cm deg⁻⁵. Then

$$a = \left[\frac{\theta(\text{Cu})}{\theta(\text{Ag})}\right]^5 (2.6 \times 10^{-16}) = 20.4 \times 10^{-16} \frac{\text{ohm cm}}{\text{deg}^5}$$

Values of ρ_s shown in tables VI and VII have been found, using for a temperature T_2 , a value near the resistance minimum. The results for our alloys have been plotted against $\log_e(T_1/T_2)$ in figure 14.

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TABLE VI

0.31 at % Mn

$$T_2 = 13.0^\circ \text{K}$$

$$\rho(T_2) = .508 \mu\text{ohm cm}$$

$T_1, ^\circ\text{K}$	$\rho(T_1) - \rho(T_2) \text{ ohm cm}$	$a(T_2^5 - T_1^5) \text{ ohm cm}$	$\rho_s \text{ ohm cm}$	$\log_e \frac{T_1}{T_2}$
10.86	10×10^{-10}	4.6×10^{-10}	14.6×10^{-10}	-.18
9.05	17	6.1	23.1	-.36
6.25	53	7.2	60.1	-.73
6.79	42	7	49	-.65
16.8	11	-19.8	-8.8	+.25
18.7	18	-39.2	-21.2	+.36

0.067 at % Mn

$$T_2 = 9.8^\circ \text{K}$$

$$\rho(T_2) = 9.30 \times 10^{-8} \text{ ohm cm}$$

$T_1, ^\circ\text{K}$	$\rho(T_1) - \rho(T_2) \text{ ohm cm}$	$a(T_2^5 - T_1^5) \text{ ohm cm}$	$\rho_s \text{ ohm cm}$	$\log \frac{T_1}{T_2}$
8.15°K	0.03×10^{-8}	0.010×10^{-8}	4×10^{-10}	-.18
6.91	.07	.015	8.5	-.34
5.58	.11	.017	12.7	-.56
4.13	.18	.018	19.8	-.86
3.61	.25	.018	26.8	-1.00
3.45	.24		25.8	-1.04
2.93	.32		33.8	-1.20
2.78	.31		32.8	-1.26
2.28	.37		38.8	-1.45
2.03	.36		37.8	-1.57
1.91	.35		36.8	-1.63

TABLE VII

0.11 at % Mn

$T_2 = 12.0^\circ \text{K}$

$\rho(T_2) = .1786 \mu\text{ohm cm.}$

T_1	$\rho(T_1) - \rho(T_2)$	$a (T_2^5 - T_1^5) \text{ ohm cm}$	$\rho_s \text{ ohm cm}$	$\log \frac{T_1}{T_2}$
10.2°K	$3 \times 10^{-10} \text{ ohm cm}$	2.8×10^{-10}	5.8×10^{-10}	-.16
8.68	13	3.7	16.7	-.32
6.82	24	4.7	28.7	-.56
6.19	30	5.0	35	-.66
4.14	41	5.1	46	-1.06
3.64	44	"	49	-1.19
3.17	47	"	52	-1.34
2.71	45		50	-1.49
15.5	4	-13.2	- 8.8	+.26
18.7	24	-42.0	-18	+.44

0.005 at % Mn

$T_2 = 6.5^\circ \text{K}$

$\rho(T_2) = 1.102 \times 10^{-8} \text{ ohm cm.}$

T_1	$\rho(T_1) - \rho(T_2)$	$a (T_2^5 - T_1^5) \text{ ohm cm}$	$\rho_s \text{ ohm cm}$	$\log \frac{T_1}{T_2}$
4.83°K	$0.005 \times 10^{-8} \text{ ohm cm}$	0.18×10^{-10}	0.68×10^{-10}	-.30
4.12	.009	.22	1.12	-.45
3.75	.011	.23	1.33	-.55
3.36	.013	.24	1.54	-.66
2.86	.019	.24	2.14	-.82
2.32	.028	.24	3.04	-1.03
1.84	.039	.24	4.14	-1.26
7.60	.002	-.28	-.08	+.15
8.26	.002	-.55	-.35	+.24
9.12	.003	-1.05	-.75	+.34
11.28	.014	-3.5	- 2.1	+.55

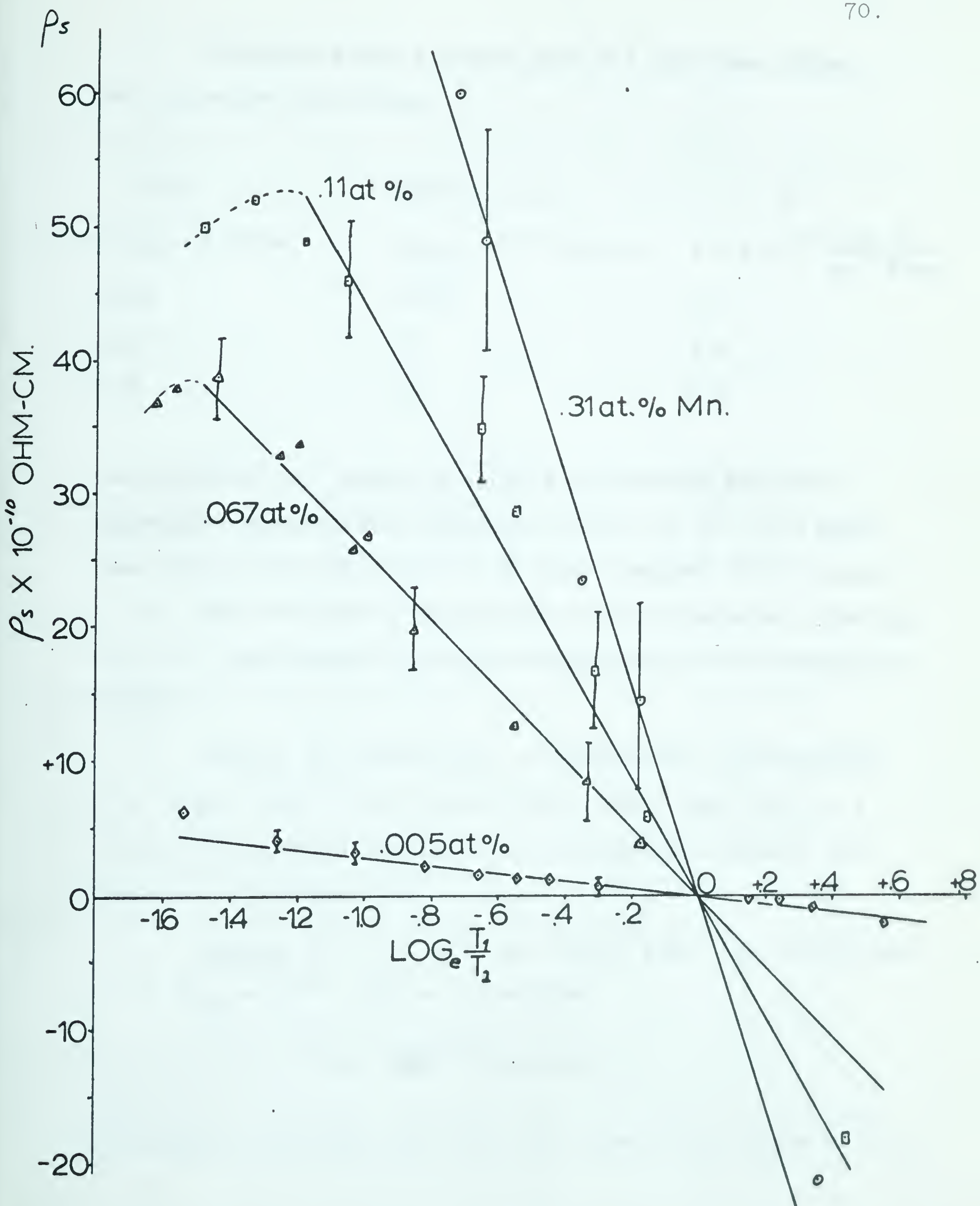


FIGURE 14

Straight lines giving a good fit have been drawn.

The slopes are as follows:

Alloy	Slope = $-c\rho'$	ρ'
0.005 ₂ at. % Mn	-2.5×10^{-10} ohm cm.	$4.8 \times 10^{-8} \frac{\text{ohm cm}}{\text{at. \% Mn}}$
0.067	-26.5	4.0
0.11	-43	3.9
0.31	-79	2.6

The values of ρ' agree quite well considering that the manganese concentration varies by a factor of 20. The small value of ρ' for the 0.31 at. % alloy compared to the values of ρ' for the other alloys may be due to a magnetic ordering effect at temperatures below the temperature of the resistance minimum.

Figure 14 should not be considered a confirmation of a $\log_e T$ term in the resistivity. When $\log_e T_1/T_2 < 1$, the plot is rather insensitive to the algebraic form of the anomalous resistance term.

Taking $\rho' = 4 \times 10^{-8}$ ohm cm/at. % Mn the coefficient D in $T_{\min} = Dc^{1/5}$ may be calculated

$$D = \left(\frac{\rho'}{5a}\right)^{1/5} = 21.$$

This agrees reasonably well with the experimental value of 18.5.

The experimental coefficient of resistivity increase for Mn as an impurity is 1.60×10^{-6} ohm cm/at.%. If, as Kondo says, ρ_m and ρ_A are about equal, then one can find J. Say $\rho_m = 0.8 \times 10^{-6}$ ohm cm/at.% Mn. Then, since

$$\rho' = - \frac{3zJ\rho_m}{E_F},$$

we obtain $J \approx -0.08$ eV. This is about 0.4 of the value of J obtained for iron in gold.

Notice that J is negative, which agrees with the sign of J determined earlier to explain a positive thermoelectric power in these alloys at very low temperatures.

Qualitative evidence for the statement that the electrical resistance minimum and maximum are two separate effects comes from the specific heat anomaly reported by de Nobel and du Chatenier (1959) for manganese-silver alloys. The extra contribution to the specific heat over that of pure silver becomes noticeable at a temperature just below $T_{\max}$ for each alloy while there is no contribution to the specific heat at a temperature corresponding to the resistance minimum temperature $T_{\min}$.

The thermoelectric power of our alloys is of the order of 30 times that expected from a simple electron diffusion term given by equation (8). At 5°K the magnitude of the diffusion thermopower is less than 0.1×10^{-6} $\mu\text{V}/\text{deg}$.

while the observed thermoelectric power was of the order of -2 to -3 $\mu\text{V}/\text{deg}$. The thermoelectric power of a specimen with no manganese in solution was positive and less than 1.0 $\mu\text{V}/\text{deg}$. in agreement with Pearson (1961). This positive contribution arises from the phonon drag effect which has a maximum at about 40° K in silver. The fact that the phonon drag thermoelectric power is positive means that the effect of Umklapp phonon-electron collisions dominates the effect of the Normal collisions in the thermoelectric power.

The positive term in the thermoelectric power at very low temperatures in the alloys with the largest amounts of manganese has already been explained in terms of a ferromagnetic ordering of magnetic ion spins. In the region of large negative "giant" thermoelectric powers, especially with the more dilute alloys, there is no magnetic evidence for any ordering of the spins. In the 0.005 at. % Mn alloy (50 parts per million) the average interatomic spacing of the manganese atoms is 27 silver atoms. Certainly, unless some sort of super exchange force is present, the manganese atoms in solution must be in a paramagnetic state. Phonon processes must also be ruled out from causing the "giant" thermoelectric power because firstly the observed thermoelectric power S is too large in magnitude and secondly S does not approach zero as the temperature approaches zero as it should when fewer and fewer phonons are excited.

Figure 14 shows a plot of thermoelectric power at 7°K as a function of the inverse residual resistance ratio. When there is more than one contribution to the diffusion thermoelectric power S_e , then

$$S_e = \frac{\sum W_i S_i}{\sum W_i} \quad (10)$$

In the residual resistance region with two terms in S , then

$$S_e = \frac{W_1 S_1 + W_2 S_2}{W_1 + W_2} = \frac{\rho_1 S_1 + \rho_2 S_2}{\rho_1 + \rho_2} = S_2 + (S_1 - S_2) \frac{\rho_1}{\rho} \quad (17)$$

where W_1 , ρ_1 , S_1 are characteristic of a non-magnetic impurity

and W_2 , ρ_2 , S_2 are characteristic of a magnetic impurity.

The results for the less dilute alloys lie on a straight line while the 0.005 at. % Mn result does not. This is in general agreement with the thermoelectric power results of other resistance minimum alloys measured by MacDonald, Pearson, and Templeton (1962).

Manganese in solution in silver has a characteristic thermoelectric power of about -1.1 $\mu\text{V}/\text{deg}$ at 7°K for all but the most dilute concentrations. The apparent break in the graph of figure 14 indicates a thermoelectric power

from only one term in equation (17).

The thermoelectric power of the more dilute alloys has a temperature independent region. This agrees with the prediction by Kondo (1964b) that the thermoelectric power of dilute magnetic alloys is independent of both the impurity concentration c and the temperature in the residual resistance region. This is a result of a localized s-d interaction increasing the density of states at the Fermi surface. Kondo obtains the following expression for the thermoelectric power:

$$S = - \frac{k}{e} 2\pi Z \frac{N(E_F)}{N} \frac{\rho_0}{\rho_0 + \rho_i} \quad (18)$$

where Z is an imaginary term in the impurity potential and $\frac{N(E_F)}{N}$ is the density of states at the Fermi surface.

Kondo obtains $Z \approx 0.09$ electron volts (eV) with $\frac{N(E_F)}{N} \sim 0.1$ for copper-manganese alloys. If the density of states is the same in silver-manganese alloys then $Z \approx 0.05$ electron volts.

The thermoelectric power of all the samples becomes positive in the range 22-28°K. This is due to the additive contribution of the phonon drag thermoelectric power in pure silver. It is interesting to note that S in the

more dilute alloys becomes positive at lower temperatures. This fact is likely due to the damping out of the anomalous term in S by a lattice resistance that, at 15°K , is substantial compared to the residual resistance (see equation (18)).

IV.2 Summary

The addition of manganese to silver in dilute amounts produces a minimum and a maximum in the electrical resistivity at low temperatures. The minimum and the maximum are due to two different effects because the variation with manganese concentration of the temperature at which the minimum occurs is different from the variation with concentration of the temperature at which the maximum occurs. The electrical resistance minimum was also observed in the thermal resistance - temperature product $W_e T$ of the 0.005 at. % Mn alloy. However for the alloys with the largest amounts of manganese in solution no link between the thermal conductivity anomaly and the resistance anomaly below T_{max} , the temperature of the maximum, could be definitely established on the basis of theories used for dilute alloys with non-magnetic impurities. The general conclusion is that the resistance minimum arises from elastic electron scattering processes and the resistance maximum arises from inelastic

scattering processes. We also suggest that the cooperative interaction between manganese ions in solution which causes inelastic scattering also causes the positive thermoelectric power at very low temperatures.

The temperature of the resistance minimum $T_{\min}$ varies with manganese concentration as c^m with m falling in the range $m^{-1} = 5.0$ to 5.5 and also $T_{\min}$ varies linearly with the Debye temperature of the solvent.

The most promising model to explain the electrical resistance minimum has been worked out by Kondo (1964a) using the second Born approximation in the scattering of electrons by magnetic impurities. Kondo (1964b) can also explain the large negative thermoelectric power of resistance minimum alloys by using an imaginary term in the impurity potential.

It is known (and predicted by Yosida (1957)) that the quantity $\Delta\rho = \rho(T_{\max}) - \rho(T=0)$ is proportional to the concentration c of manganese for alloys with about one percent manganese in silver and copper. It would be interesting to check this by measuring the resistivity of the alloys used in this work down to say 0.3°K (He^3 cryostat). A measurement of the resistivity of the 0.005 at. % Mn alloy to such a temperature would give a more definite measure of whether or not there is a logarithmic singularity in the resistivity as Kondo predicts.

The method used for preparing the alloys should be particularly useful for preparing alloys with a small solid solubility. For instance, Knook and Van den Berg (1960) have observed that molybdenum in gold produces a resistance minimum. Although molybdenum probably does not form equilibrium solid solutions with the noble metals, such alloys would probably exhibit resistance minima. Chill casting from the well-mixed melts produced by an induction furnace could produce alloys with greater molybdenum concentrations than the solid solubility limit.

Recently Coles (1964) reported a resistance anomaly in rhodium containing small amounts of iron. Small amounts of iron seem to produce an abnormal decrease in the resistance below 30°K , at which temperature the resistance should have reached its constant residual value. It would be interesting to study the thermoelectric power and thermal conductivity of alloys with rhodium as a solvent and certain transition metals as solutes to see if any correlation with resistance minimum alloys exists.

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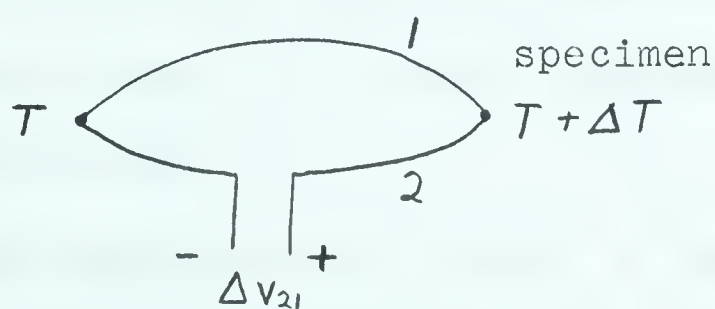
APPENDIX

Determination of the Absolute Thermoelectric Power

When a temperature gradient is applied to a conductor there is, together with a heat flow, a flow of electric current known as the thermoelectric current. This current can be measured only in a closed circuit of some sort. This circuit must consist of conductors with different thermoelectric properties since, by symmetry, no thermoelectric current will flow in a circuit of a single conductor. This leads to the problem of finding the absolute thermoelectric power S of a conductor.

$$S = \frac{dV}{dT} \approx \frac{\Delta v}{\Delta T}$$

The measuring circuit is as shown below



If $\Delta T \ll T$ then the voltage measured $\Delta v_{21} \propto \Delta T$. Conductors 1 and 2 have characteristic thermoelectric powers S_1 and S_2 respectively. Since Δv_{21} is the algebraic sum of two voltage differences due to S_1 in conductor 1 and S_2 in conductor 2,

$$\Delta v_{21} = \Delta v_2 - \Delta v_1 = (S_2 - S_1)\Delta T$$

$$S_2 - S_1 = \frac{\Delta v_{21}}{\Delta T}$$

By definition, with the polarity of Δv_{21} as shown and with $\Delta T > 0$ then $S_2 - S_1 = \Delta v_{21}/\Delta T > 0$ or $S_2 > S_1$. If the thermoelectric power of conductor 2 can be neglected, then a good rule of thumb is the following:

- a) if the "hot" end of the conductor 1 is negative (with respect to the "cool" end), then S_1 is positive
- b) if the "hot" end of conductor 1 is positive, then S_1 is negative.

Since a superconductor has no thermoelectric power, it is possible to determine the absolute thermoelectric power of the sample by direct means at low enough temperatures. At higher temperatures indirect means must be used.

The thermoelectric power S of a conductor can be used to give the Thomson heat of a conductor μ and the Peltier heat π of a conductor by use of the Kelvin relations,

$$\mu = T \frac{dS}{dT}$$

$$\text{and} \quad \pi = TS.$$

Integrating the relation for μ

$$S(T) - S(0) = \int_0^T \frac{\mu}{T} dT .$$

From the third law of thermodynamics the thermoelectric properties vanish as $T \rightarrow 0$. This enables the determination of S at high temperatures.

The absolute thermoelectric power of Lead (Pb) has been determined over a complete temperature range.

1. Above 20°K. Borelius et al. (1932) have determined S by measurement of the Thomson heat μ .
2. Below 18°K. Christian et al. (1958) have determined S for Pb relative to a superconductor.

(the symbol Pb is used for the element lead to differentiate from electrical leads). In order to deduce the contribution to the thermoelectric power of conductor 2, the leads in the cryostat, a specimen of Pb wire was made. By comparing the measured values of the thermoelectric power and the published values for the absolute thermoelectric power of Pb, the thermoelectric power of the lead wires was deduced. The thermal conductivity was easily measured at the same time.

The Pb was extruded in the form of a wire 0.040 inch in diameter. Cominco Pb shot, 59 grade was used.

The potential and current contacts were soldered to the Pb wire with Pb solder.

The results on the thermoelectric power and thermal conductivity are given in table VIII. The results for the thermal conductivity of the Pb and the deduced thermoelectric power of the lead wires are shown in figure 15 . The convention used to determine the absolute thermoelectric power of the sample is illustrated in the following example.

In the 0.31 at. % Mn alloy at $T = 11.21^{\circ}\text{K}$, the measured value of S was $-1.42 \mu\text{v}/\text{deg}$. The absolute thermoelectric power of the sample was then $(-1.42 + 0.14) = -1.28 \mu\text{v}/\text{deg}$. Here $0.14 \mu\text{v}/\text{deg}$ at 11.2°K is determined from figure 15.

TABLE VIII

Lead (Pb) Wire

Temperature T	Thermal Conductivity	Measured S	S of Leads ($S_{\text{meas}} - S_{\text{Pb}}$)
3.30°K	3.26 $\frac{\text{watts}}{\text{deg.cm}}$	0.00	0
3.77	3.17	0	0
4.27	3.05	+0.035 $\frac{\mu\text{v}}{\text{deg}}$	+0.035 $\frac{\mu\text{v}}{\text{deg}}$
6.37	3.32	+0.08	+0.08
6.73	3.47	+0.07	+0.07
7.99	3.26	-0.42	-0.17
8.08	3.40	-0.36	-0.10
9.73	2.17	-0.52	-0.12
11.1	1.525	-0.66	-0.14
13.2	1.20	-0.89	-0.23
15.9	0.848	-0.96	-0.19
18.9	0.796	-1.14	-0.36
22.9	0.707	-1.35	-0.57
25.2	0.660	-1.60	-0.83

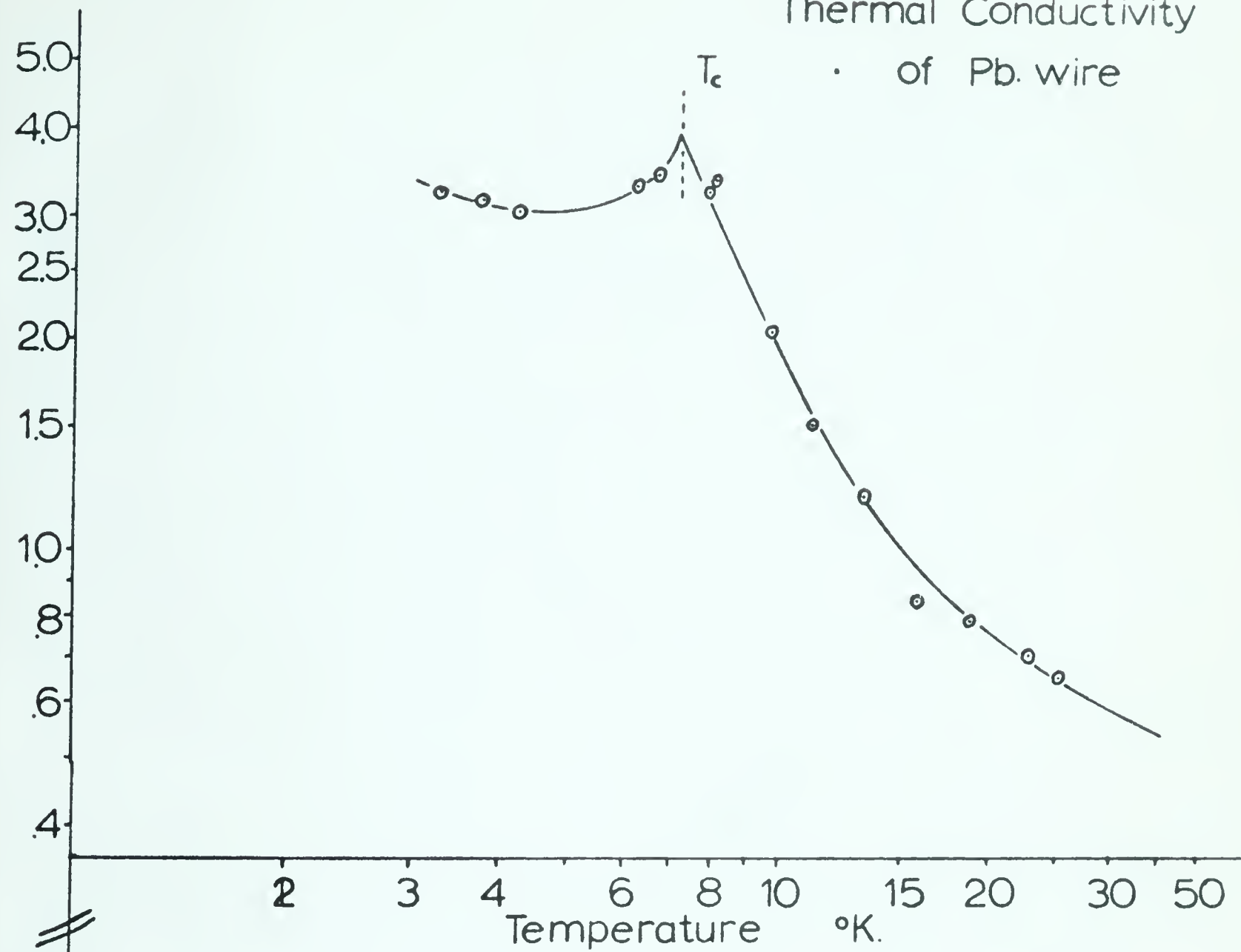
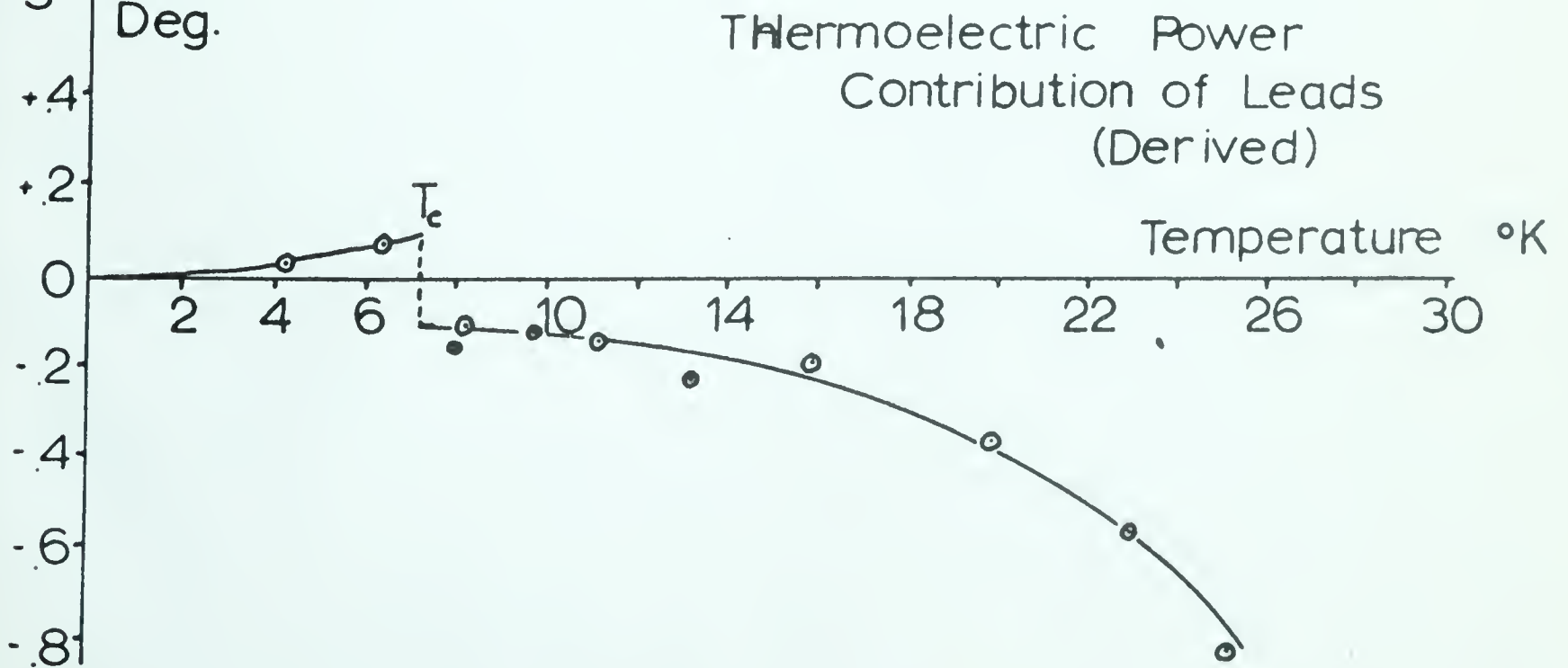
$\lambda \frac{\text{Watts}}{\text{Deg.Cm.}}$

 $S \frac{\mu\text{V}}{\text{Deg.}}$


Figure 15

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